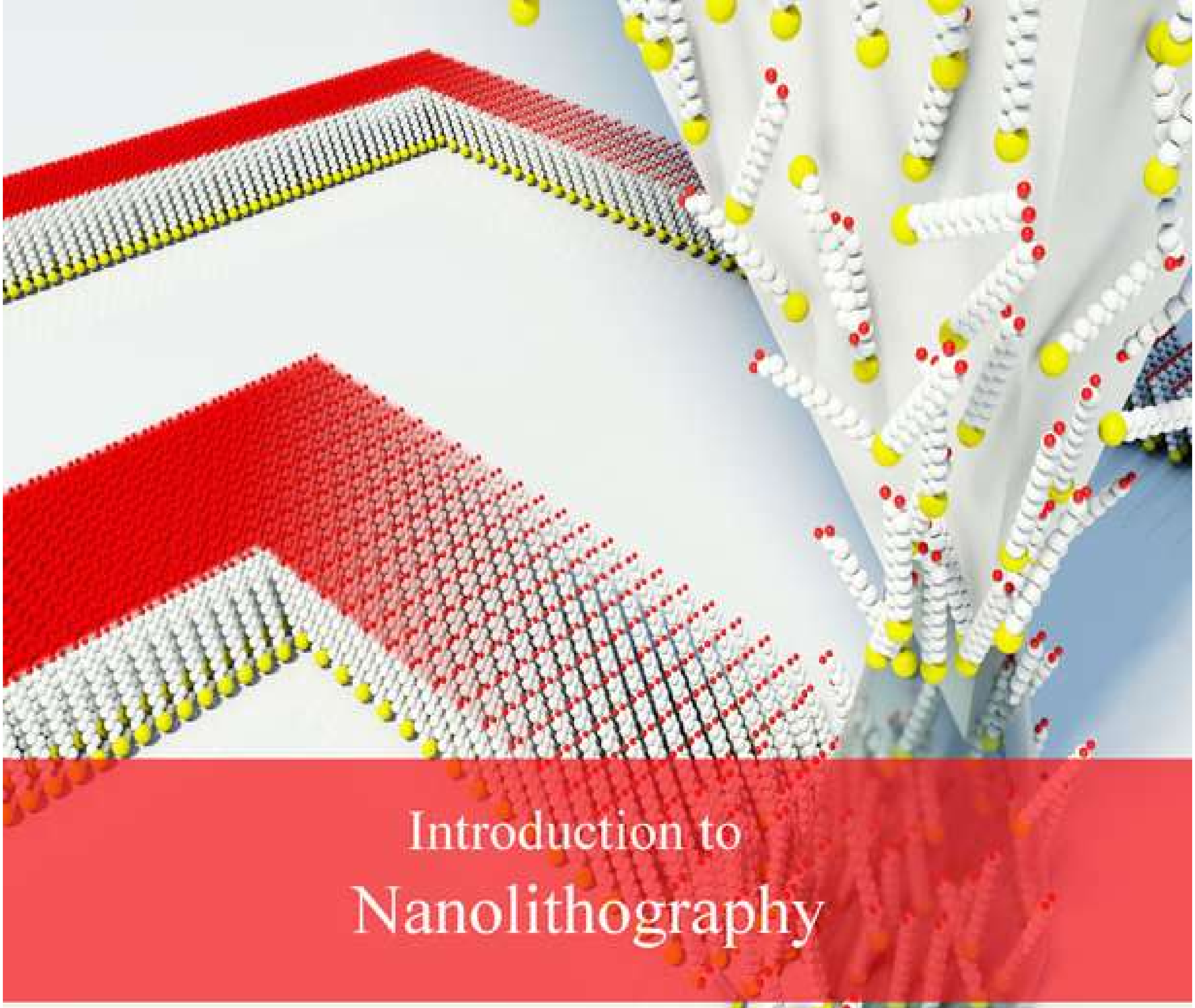

Introduction to
Nanolithography

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Table of Contents

Chapter 1- Introduction to Nanolithography

Chapter 2 - Multiple Patterning

Chapter 3 - Electron Beam Lithography

Chapter 4 - Extreme Ultraviolet Lithography

Chapter 5 - Nanoimprint Lithography

Chapter 6 - Local Oxidation Nanolithography

Chapter 7 - Dip-Pen Nanolithography

Chapter 8 - Other Techniques of Nanolithography

Chapter- 1

Introduction to Nanolithography

Nanolithography is the branch of nanotechnology concerned with the study and application of fabricating nanometer-scale structures, meaning patterns with at least one lateral dimension between the size of an individual atom and approximately 100 nm. Nanolithography is used during the fabrication of leading-edge semiconductor integrated circuits (nanocircuitry) or nanoelectromechanical systems (NEMS).

As of 2007, nanolithography is a very active area of research in academia and in industry.

Optical lithography

Optical lithography, which has been the predominant patterning technique since the advent of the semiconductor age, is capable of producing sub-100-nm patterns with the use of very short wavelengths (currently 193 nm). Optical lithography will require the use of liquid immersion and a host of resolution enhancement technologies (phase-shift masks (PSM), optical proximity correction (OPC)) at the 32 nm node. Most experts feel that traditional optical lithography techniques will not be cost effective below 22 nm. At that point, it may be replaced by a next-generation lithography (NGL) technique.

Photolithography (or "optical lithography") is a process used in microfabrication to selectively remove parts of a thin film or the bulk of a substrate. It uses light to transfer a geometric pattern from a photo mask to a light-sensitive chemical "photoresist", or simply "resist," on the substrate. A series of chemical treatments then engraves the exposure pattern into the material underneath the photo resist. In complex integrated circuits, for example a modern CMOS, a wafer will go through the photolithographic cycle up to 50 times.

Photolithography shares some fundamental principles with photography in that the pattern in the etching resist is created by exposing it to light, either using a projected image or an optical mask. This procedure is comparable to a high precision version of the method used to make printed circuit boards. Subsequent stages in the process have more in common with etching than to lithographic printing. It is used because it affords exact control over the shape and size of the objects it creates, and because it can create patterns over an entire surface simultaneously. Its main disadvantages are that it requires a flat substrate to start with, it is not very effective at creating shapes that are not flat, and it can require extremely clean operating conditions.

Basic procedure

The wafer track portion of an aligner that uses 365 nm ultraviolet light.

A single iteration of photolithography combines several steps in sequence. Modern cleanrooms use automated, robotic wafer track systems to coordinate the process. The procedure described here omits some advanced treatments, such as thinning agents or edge-bead removal.

Cleaning

If organic or inorganic contaminations are present on the water surface, they are usually removed by wet chemical treatment, e.g. the RCA clean procedure based on solutions containing hydrogen peroxide.

Preparation

The wafer is initially heated to a temperature sufficient to drive off any moisture that may be present on the wafer surface. Wafers that have been in storage must be chemically cleaned to remove contamination. A liquid or gaseous "adhesion promoter", such as Bis(trimethylsilyl)amine ("hexamethyldisilazane", HMDS), is applied to promote adhesion of the photoresist to the wafer. The phrase "adhesion promoter" is a misnomer, as the surface layer of silicon dioxide on the wafer reacts with the agent to form Methylated Silicon-hydroxide, a highly water repellent layer not unlike the layer of wax on a car's paint. This water repellent layer prevents the aqueous developer from penetrating between the photoresist layer and the wafer's surface, thus preventing so-called lifting of small photoresist structures in the (developing) pattern.

Photoresist application

The wafer is covered with photoresist by spin coating. A viscous, liquid solution of photoresist is dispensed onto the wafer, and the wafer is spun rapidly to produce a uniformly thick layer. The spin coating typically runs at 1200 to 4800 rpm for 30 to 60 seconds, and produces a layer between 0.5 and 2.5 micrometres thick. The spin coating process results in a uniform thin layer, usually with uniformity of within 5 to 10 nanometres. This uniformity can be explained by detailed fluid-mechanical modelling, which shows that the resist moves much faster at the top of the layer than at the bottom, where viscous forces bind the resist to the wafer surface. Thus, the top layer of resist is quickly ejected from the wafer's edge while the bottom layer still creeps slowly radially along the wafer. In this way, any 'bump' or 'ridge' of resist is removed, leaving a very flat layer. Final thickness is also determined by the evaporation of liquid solvents from the resist. For very small, dense features (<125 or so nm), thinner resist thicknesses (<0.5 micrometres) are needed to overcome collapse effects at high aspect ratios; typical aspect ratios are <4:1.

The photo resist-coated wafer is then prebaked to drive off excess photoresist solvent, typically at 90 to 100 °C for 30 to 60 seconds on a hotplate.

Exposure and developing

After prebaking, the photoresist is exposed to a pattern of intense light. Optical lithography typically uses ultraviolet light (see below). Positive photoresist, the most common type, becomes soluble in the basic developer when exposed; exposed negative photoresist becomes insoluble in the (organic) developer. This chemical change allows some of the photoresist to be removed by a special solution, called "developer" by analogy with photographic developer. To learn more about the process of exposure and development of positive resist, see: Ralph Dammel, "Diazonaphtoquinone-based resists", SPIE Optical Engineering Press, Vol TT11 (1993).

A PEB (post-exposure bake) is performed before developing, typically to help reduce standing wave phenomena caused by the destructive and constructive interference patterns of the incident light. In DUV (deep ultraviolet, or 248 nm exposure wavelength) lithography, CAR (chemically amplified resist) chemistry is used. This process is much more sensitive to PEB time, temperature, and delay, as most of the "exposure" reaction (creating acid, making the polymer soluble in the basic developer) actually occurs in the PEB.

The develop chemistry is delivered on a spinner, much like photoresist. Developers originally often contained sodium hydroxide (NaOH). However, sodium is considered an extremely undesirable contaminant in MOSFET fabrication because it degrades the insulating properties of gate oxides (specifically, sodium ions can migrate in and out of the gate, changing the threshold voltage of the transistor and making it harder or easier to turn the transistor on over time). Metal-ion-free developers such as tetramethylammonium hydroxide (TMAH) are now used.

The resulting wafer is then "hard-baked" if a non-chemically amplified resist was used, typically at 120 to 180 °C for 20 to 30 minutes. The hard bake solidifies the remaining photoresist, to make a more durable protecting layer in future ion implantation, wet chemical etching, or plasma etching.

Etching

In etching, a liquid ("wet") or plasma ("dry") chemical agent removes the uppermost layer of the substrate in the areas that are not protected by photoresist. In semiconductor fabrication, dry etching techniques are generally used, as they can be made anisotropic, in order to avoid significant undercutting of the photoresist pattern. This is essential when the width of the features to be defined is similar to or less than the thickness of the material being etched (i.e. when the aspect ratio approaches unity). Wet etch processes are generally isotropic in nature, which is often indispensable for microelectromechanical systems, where suspended structures must be "released" from the underlying layer.

The development of low-defectivity anisotropic dry-etch process has enabled the ever-smaller features defined photolithographically in the resist to be transferred to the substrate material.

Photoresist removal

After a photoresist is no longer needed, it must be removed from the substrate. This usually requires a liquid "resist stripper", which chemically alters the resist so that it no longer adheres to the substrate. Alternatively, photoresist may be removed by a plasma containing oxygen, which oxidizes it. This process is called ashing, and resembles dry etching.

Exposure ("printing") systems

Exposure systems typically produce an image on the wafer using a photomask. The light shines through the photomask, which blocks it in some areas and lets it pass in others.

(Maskless lithography projects a precise beam directly onto the wafer without using a mask, but it is not widely used in commercial processes.) Exposure systems may be classified by the optics that transfer the image from the mask to the wafer.

Contact and proximity

A contact printer, the simplest exposure system, puts a photomask in direct contact with the wafer and exposes it to a uniform light. A proximity printer puts a small gap between the photomask and wafer. In both cases, the mask covers the entire wafer, and simultaneously patterns every die.

Contact printing is liable to damage both the mask and the wafer, and this was the primary reason it was abandoned for high volume production. Both contact and proximity lithography require the light intensity to be uniform across an entire wafer, and the mask to align precisely to features already on the wafer. As modern processes use increasingly large wafers, these conditions become increasingly difficult.

Research and prototyping processes often use contact lithography, because it uses inexpensive hardware and can achieve high optical resolution. The resolution is approximately the square root of the product of the wavelength and the gap distance. Hence, contact printing offers the best resolution, because its gap distance is approximately zero (neglecting the thickness of the photoresist itself). In addition, nanoimprint lithography may revive interest in this familiar technique, especially since the cost of ownership is expected to be low.

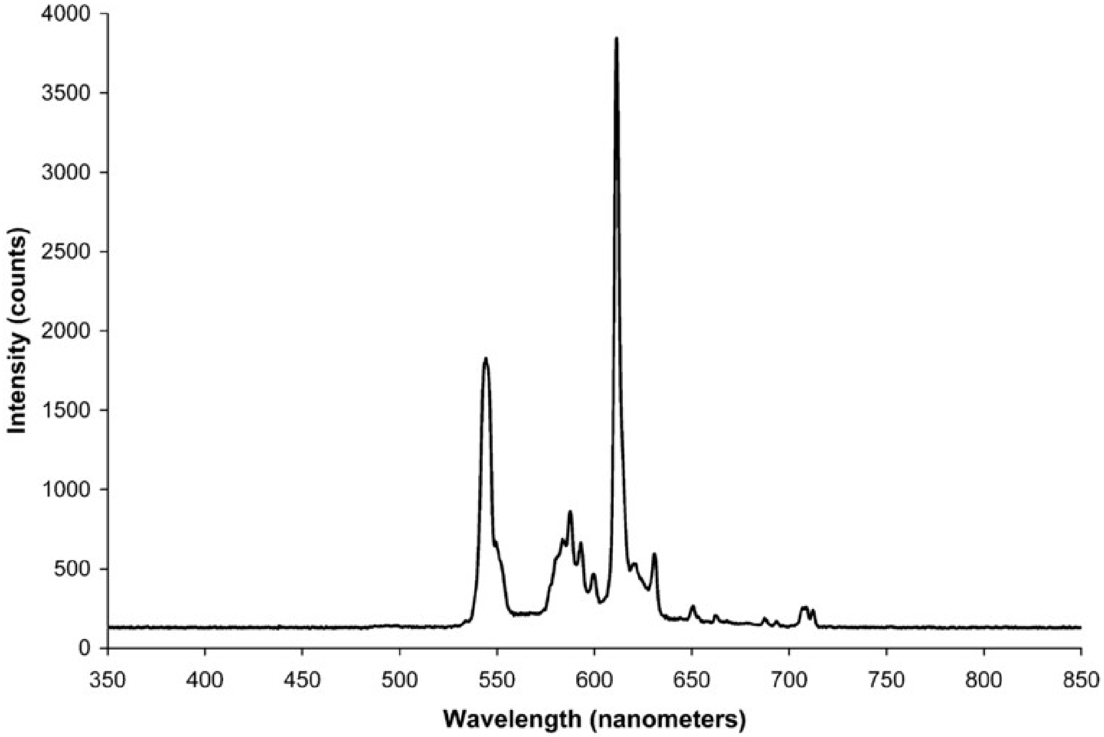
Projection

Very-large-scale integration lithography uses projection systems. Unlike contact or proximity masks, which cover an entire wafer, projection masks (known as "reticles") show only one die or an array of die (known as a "field"). Projection exposure systems (steppers) project the mask onto the wafer many times to create the complete pattern.

Photomasks

The image for the mask originates from a computerized data file. This data file is converted to a series of polygons and written onto a square fused quartz substrate covered with a layer of chrome using a photolithographic process. A laser beam (laser writer) or a beam of electrons (e-beam writer) is used to expose the pattern defined in the data file and travels over the surface of the substrate in either a vector or raster scan manner. Where the photoresist on the mask is exposed, the chrome can be etched away, leaving a clear path for the light in the stepper/scanner systems to travel through.

Resolution in projection systems



The filtered fluorescent lighting in photolithography cleanrooms contains no ultraviolet or blue light in order to avoid exposing photoresists. The spectrum of light emitted by such fixtures gives virtually all such spaces a bright yellow color.

The ability to project a clear image of a small feature onto the wafer is limited by the wavelength of the light that is used, and the ability of the reduction lens system to capture enough diffraction orders from the illuminated mask. Current state-of-the-art photolithography tools use deep ultraviolet (DUV) light with wavelengths of 248 and 193 nm, which allow minimum feature sizes down to 50 nm.

The minimum feature size that a projection system can print is given approximately by:

$$CD = k_1 \cdot \frac{\lambda}{NA}$$

where

CD is the **minimum feature size** (also called the **critical dimension**, *target design rule*). It is also common to write 2 *times* the *half-pitch*.

k_1 (commonly called *k1 factor*) is a coefficient that encapsulates process-related factors, and typically equals 0.4 for production. The minimum feature size can be reduced by decreasing this coefficient through Computational lithography.

λ is the wavelength of light used

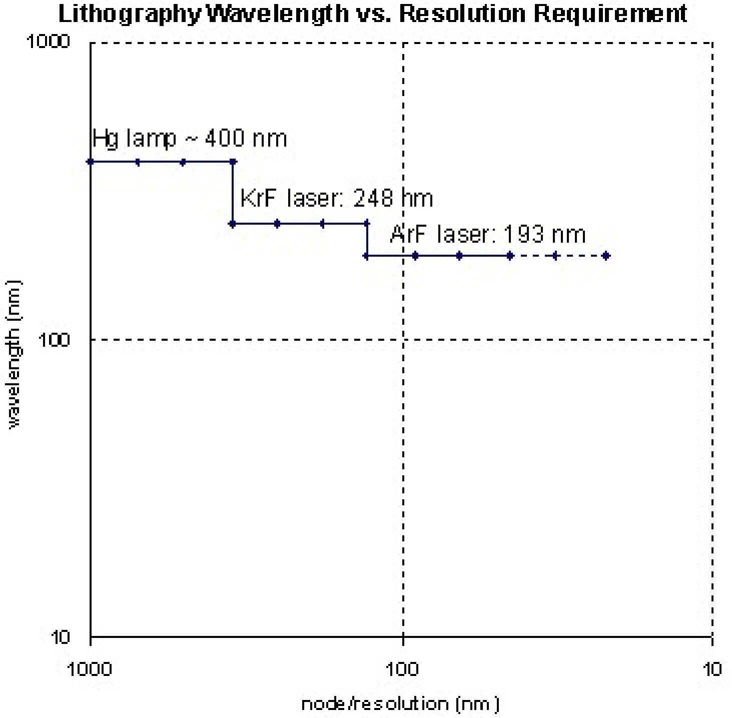
NA is the numerical aperture of the lens as seen from the wafer

According to this equation, minimum feature sizes can be decreased by decreasing the wavelength, and increasing the numerical aperture (to achieve a tighter focused beam and a smaller spot size). However, this design method runs into a competing constraint. In modern systems, the depth of focus is also a concern:

$$D_F = k_2 \cdot \frac{\lambda}{NA^2}$$

Here, k_2 is another process-related coefficient. The depth of focus restricts the thickness of the photoresist and the depth of the topography on the wafer. Chemical mechanical polishing is often used to flatten topography before high-resolution lithographic steps.

Light sources

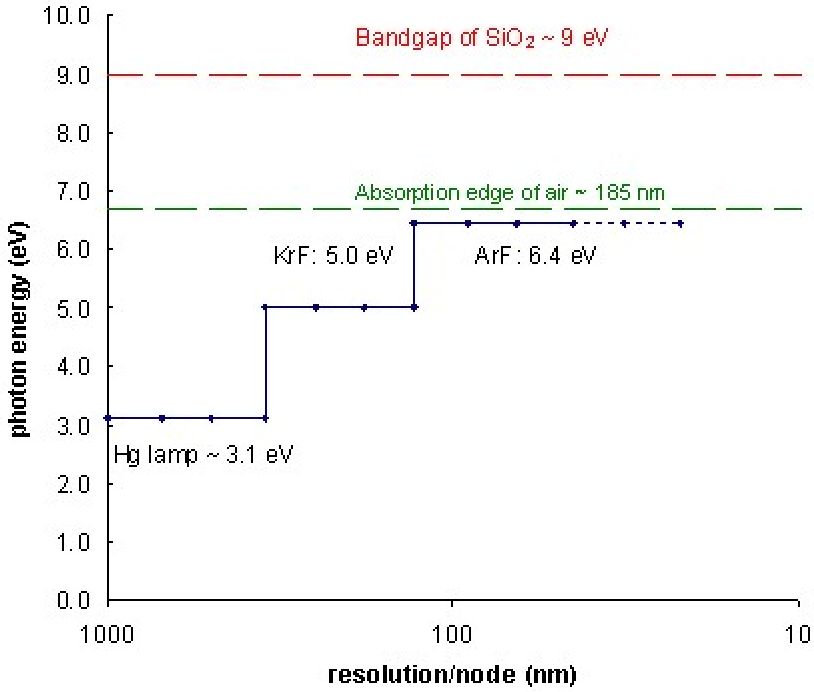


The evolution of lithography wavelength corresponding to different light sources. It is worth noting that the same light source may be used for several technology generations.

Historically, photolithography has used ultraviolet light from gas-discharge lamps using mercury, sometimes in combination with noble gases such as xenon. These lamps produce light across a broad spectrum with several strong peaks in the ultraviolet range. This spectrum is filtered to select a single spectral line, usually the "g-line" (436 nm) or "i-line" (365 nm).

More recently, lithography has moved to "deep ultraviolet", produced by excimer lasers. (In lithography, wavelengths below 300 nm are called "deep UV".) Krypton fluoride produces a 248-nm spectral line, and argon fluoride a 193-nm line. Excimer laser light sources for photolithography applications were first introduced by Cymer Inc. in the late 1980s for 248-nm wavelength lithography (KrF), and in 2001 for 193-nm wavelength lithography (ArF). Generally, changing wavelength is not a trivial matter, as the method of generating the new wavelength is completely different, and the absorption characteristics of materials change. For example, air begins to absorb significantly around the 193 nm wavelength; moving to sub-193 nm wavelengths would require installing vacuum pump and purge equipment on the lithography tools (a significant challenge). Furthermore, insulating materials such as silicon dioxide (SiO_2), when exposed to photons with energy greater than the band gap, release free electrons and holes which subsequently cause adverse charging.

Optical lithography has been extended to feature sizes below 50 nm using 193 nm and liquid immersion techniques. Also termed immersion lithography, this enables the use of optics with numerical apertures exceeding 1.0. The liquid used is typically ultra-pure, deionised water, which provides for a refractive index above that of the usual air gap between the lens and the wafer surface. The water is continually circulated to eliminate thermally-induced distortions. Water will only allow *NA*'s of up to ~1.4, but materials with higher refractive indices will allow the effective *NA* to be increased further.



Changing the lithography wavelength is significantly limited by absorption. Air absorbs below ~ 185 nm.

Experimental tools using 157 nm wavelength DUV in a manner similar to current exposure systems have been built. These were once targeted to succeed 193 nm at the 65 nm feature size node but have now all but been eliminated by the introduction of immersion lithography. This was due to persistent technical problems with the 157 nm technology and economic considerations that provided strong incentives for the continued use of 193 nm technology. High-index immersion lithography is the newest extension of 193 nm lithography to be considered. In 2006, features less than 30 nm were demonstrated by IBM using this technique.

Experimental methods

Photolithography has been defeating predictions of its demise for many years. For instance, it was predicted that features smaller than 1 micrometre could not be printed optically. Modern techniques already print features with dimensions a fraction of the wavelength of light used - an amazing optical feat. Current research is exploring new tricks in the ultraviolet regime, as well as alternatives to conventional UV, such as electron beam lithography, X-ray lithography, extreme ultraviolet lithography, ion projection lithography, and immersion lithography.

Other nanolithography techniques

- **X-ray lithography** can be extended to an optical resolution of 15 nm by using the short wavelengths of 1 nm for the illumination. This is implemented by the proximity printing approach. The technique is developed to the extent of batch processing. The extension of the method relies on Near Field X-rays in Fresnel diffraction: a clear mask feature is "demagnified" by proximity to a wafer that is set near to a "Critical Condition". This Condition determines the mask-to-wafer Gap and depends on both the size of the clear mask feature and on the wavelength. The method is simple because it requires no lenses.
- A method of pitch resolution enhancement which is gaining acceptance is **double patterning**. This technique increases feature density by printing new features in between pre-printed features on the same layer. It is flexible because it can be adapted for any exposure or patterning technique. The feature size is reduced by non-lithographic techniques such as etching or sidewall spacers.
- Work is in progress on an optical **maskless lithography** tool. This uses a digital micro-mirror array to directly manipulate reflected light without the need for an intervening mask. Throughput is inherently low, but the elimination of mask-related production costs - which are rising exponentially with every technology generation - means that such a system might be more cost effective in the case of small production runs of state of the art circuits, such as in a research lab, where tool throughput is not a concern.

- The most common nanolithographic technique is **Electron-Beam Direct-Write Lithography** (EBDW), the use of a beam of electrons to produce a pattern — typically in a polymeric resist such as PMMA.
- **Extreme ultraviolet lithography** (EUV) is a form of optical lithography using ultrashort wavelengths (13.5 nm). It is the most popularly considered NGL technique.
- **Charged-particle lithography**, such as ion- or electron-projection lithographies (PREVAIL, SCALPEL, LEEPL), are also capable of very-high-resolution patterning. Ion beam lithography uses a focused or broad beam of energetic lightweight ions (like He^+) for transferring pattern to a surface. Using Ion Beam Proximity Lithography (IBL) nano-scale features can be transferred on non-planar surfaces.
- **Neutral Particle Lithography**(NPL) uses a broad beam of energetic neutral particle for pattern transfer on a surface.
- **Nanoimprint lithography** (NIL), and its variants, such as Step-and-Flash Imprint Lithography, LISA and LADI are promising nanopattern replication technologies. This technique can be combined with **contact printing**.
- **Scanning probe lithography** (SPL) is a promising tool for patterning at the deep nanometer-scale. For example, individual atoms may be manipulated using the tip of a scanning tunneling microscope (STM). Dip-Pen Nanolithography (DPN) is the first commercially available SPL technology based on atomic force microscopy.
- **Atomic Force Microscopic Nanolithography** (AFM) is a chemomechanical surface patterning technique that uses an atomic force microscope.
- **Magnetolithography** (ML) based on applying a magnetic field on the substrate using paramagnetic metal masks call "magnetic mask". Magnetic mask which is analog to photomask define the spatial distribution and shape of the applied magnetic field. The second component is ferromagnetic nanoparticles (analog to the photoresist) that are assembled onto the substrate according to the field induced by the magnetic mask.

Bottom-up methods

- Nanosphere lithography uses self-assembled monolayers of spheres (typically made of polystyrene) as evaporation masks. This method has been used to fabricate arrays of gold nanodots with precisely controlled spacings.

It is possible that molecular self-assembly methods will take over as the primary nanolithography approach, due to ever-increasing complexity of the top-down approaches listed above. Self-assembly of dense lines less than 20 nm wide in large pre-pattearned trenches has been demonstrated. The degree of dimension and orientation control as well as prevention of lamella merging still need to be addressed for this to be an effective patterning technique. The important issue of line edge roughness is also highlighted by this technique.

Self-assembled ripple patterns and dot arrays formed by low-energy ion-beam sputtering are another emerging form of bottom-up lithography. Aligned arrays of plasmonic and magnetic wires and nanoparticles are deposited on these templates via oblique evaporation. The templates are easily produced over large areas with periods down to 25 nm.

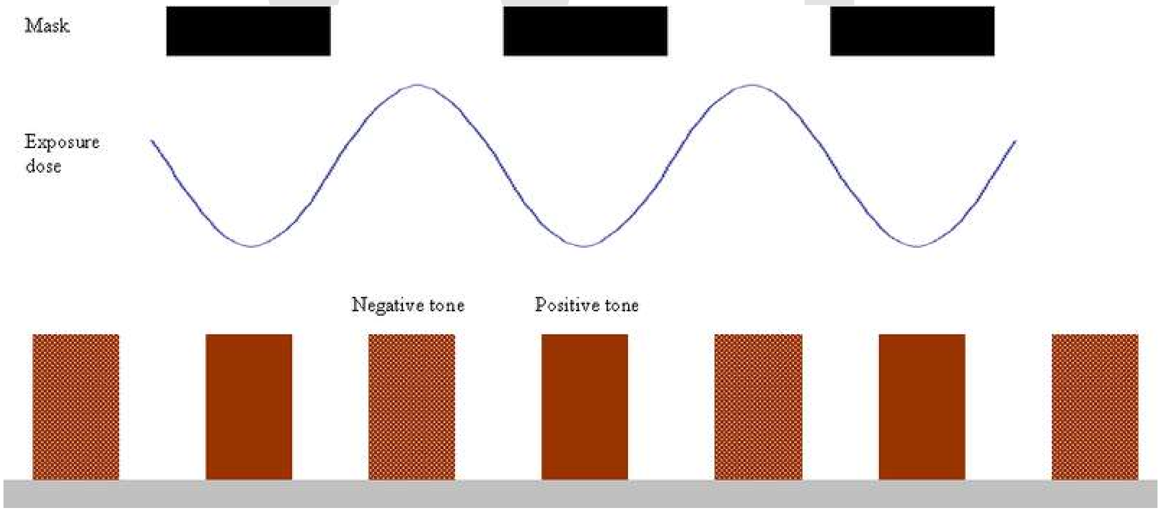
Chapter- 2

Multiple Patterning

Multiple patterning is a class of technologies developed for nanolithography to enhance the feature density. The simplest case of multiple patterning is **double patterning**, where a conventional lithography process is enhanced to produce double the expected number of features. The resolution of a photoresist pattern begins to blur at around 45 nm half-pitch. For the semiconductor industry, therefore, double patterning was introduced for the 32 nm half-pitch node and below, mainly using state-of-the-art 193 nm immersion lithography tools.

There are several types of double patterning. In combination, these may be used for multiple patterning.

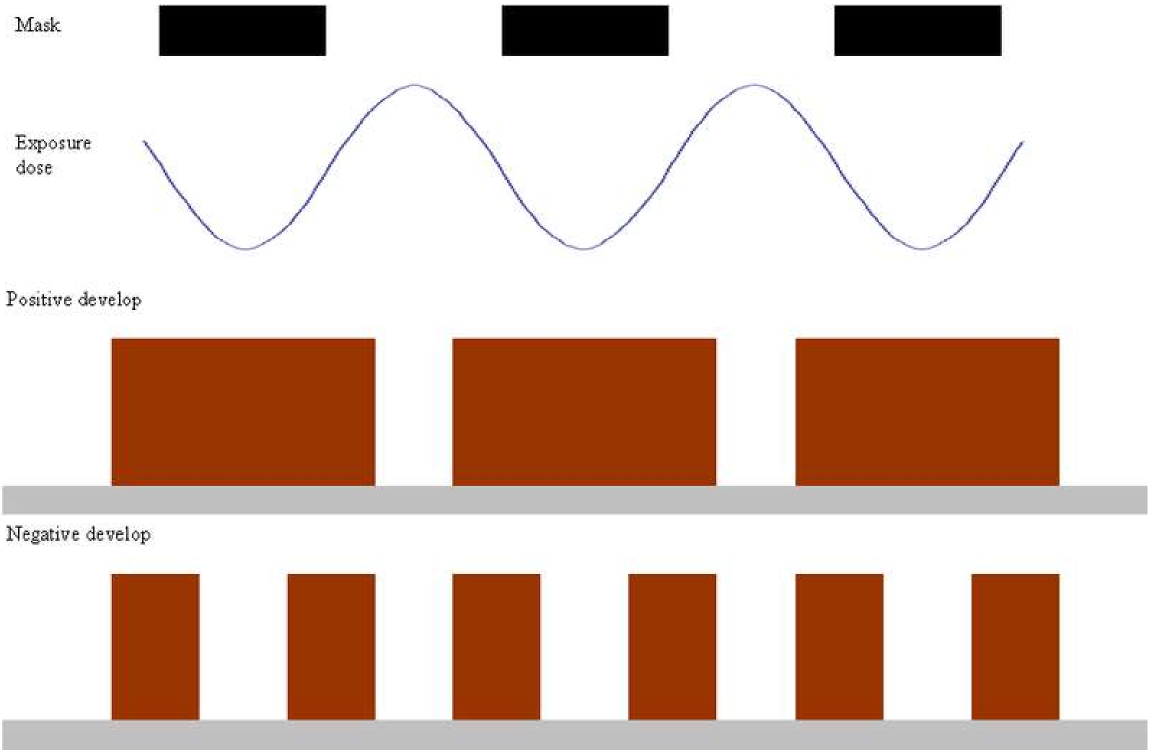
Dual-tone photoresist



Dual-tone photoresist: The lowest and highest doses of a single exposure result in insolubility, while the intermediate doses allow the photoresist to be removed by developer.

Dual-tone photoresists have been developed years ago, allowing the printing of two lines in a single exposure imaging of a single line. Early demonstrations relied on crosslinking of the highest dose regions, rendering them insoluble in developer, while the lowest dose regions were normally insoluble already. Alternatively, a photobase generator may generate acid quenchers at high doses; the acid quenching counters their ability to render the photoresist soluble. The simplicity and cost-effectiveness of this approach make it compelling as a method of extending current photolithographic capability. However, due to its inherent edge-printing characteristic, loops will generally be formed, which will need to be addressed by other process steps. In addition, the expected acid or base diffusion may limit the resolution of this technique.

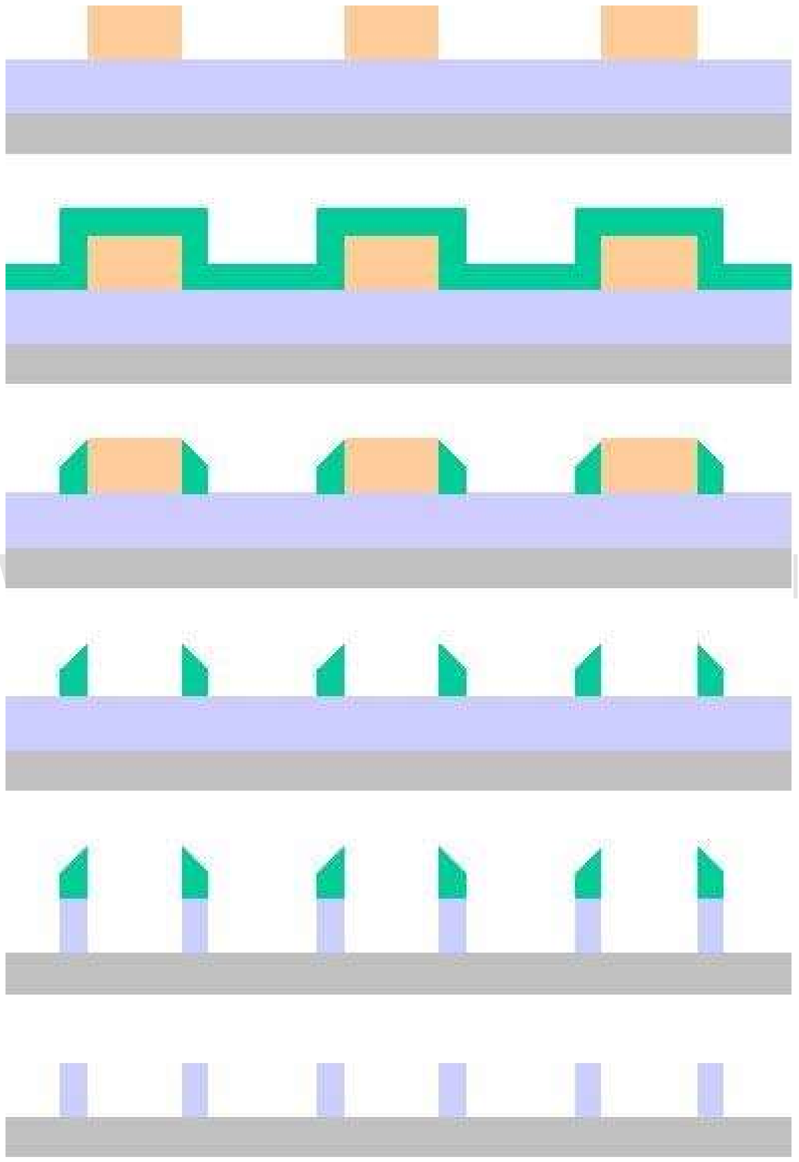
Dual-Tone Development



Dual-tone development. Two develop steps remove highest and lowest exposure dose regions of the photoresist, leaving the intermediate dose edges.

Dual-tone development, such as Fujifilm's double development process, is similar to the dual-tone photoresist technique above in that it doubles features without additional exposure. Instead the photoresist is developed twice; the first time by conventional developer which removes the high exposure dose areas, the second time by a different organic solvent which removes the unexposed or lowest exposure dose areas. This leaves the intermediate dose areas (normally defining the two feature edges) standing. A key challenge is to not only show successful positive and negative tone development process windows, but also to ensure the windows overlap sufficiently. Up to now, the successful overlap has only been shown in simulations rather than experimentally.

Self-aligned spacer



Spacer mask: first pattern; deposition; spacer formation by etching; first pattern removal; etching with spacer mask; final pattern

A spacer is a film layer formed on the sidewall of a pre-patterned feature. A spacer is formed by deposition or reaction of the film on the previous pattern, followed by etching to remove all the film material on the horizontal surfaces, leaving only the material on the sidewalls. By removing the original patterned feature, only the spacer is left. However, since there are two spacers for every line, the line density has now doubled. The spacer technique is applicable for defining narrow gates at half the original lithographic pitch, for example.

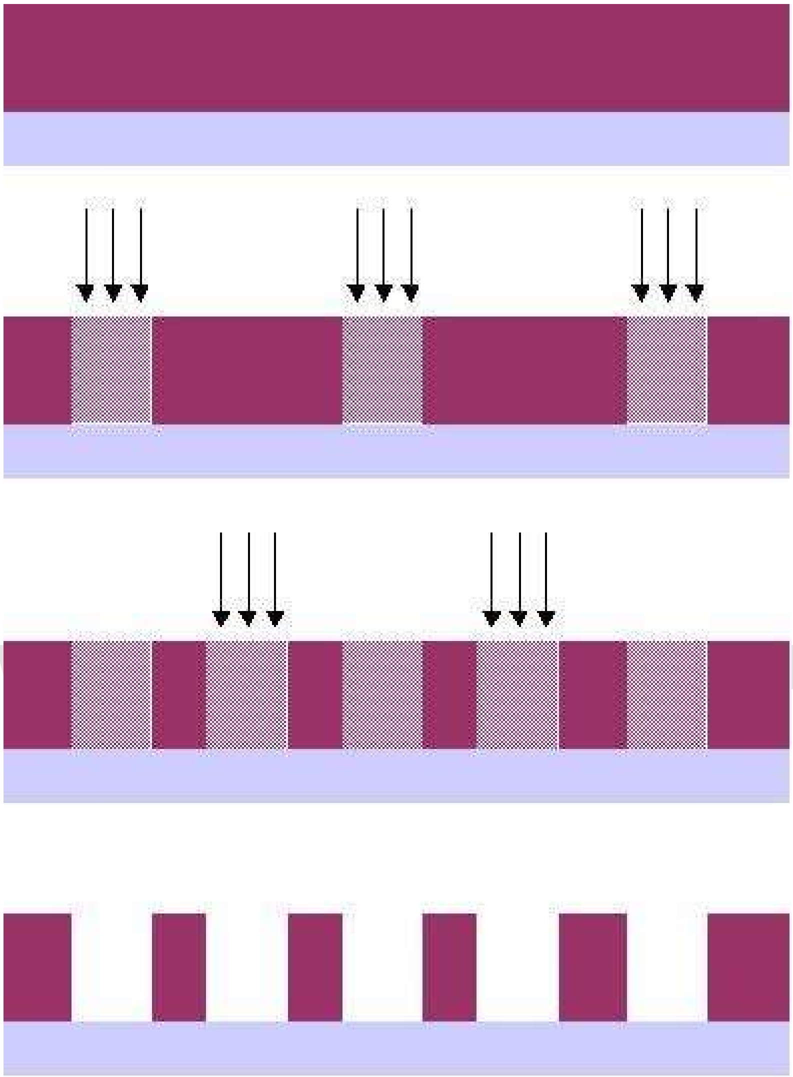
The spacer approach is unique in that with one lithographic exposure, the pitch can be halved indefinitely with a succession of spacer formation and pattern transfer processes. This conveniently avoids the serious issue of overlay between successive exposures. The spacer lithography technique has most frequently been applied in patterning fins for FinFETs.

As spacer materials are commonly hardmask materials, their post-etch pattern quality tends to be superior compared to photoresist profiles after etch, which are generally plagued by line edge roughness.

The main issues with the spacer approach are whether the spacers can stay in place after the material to which they are attached is removed, whether the spacer profile is acceptable, and whether the underlying material is attacked by the etch removing the material attached to the spacer. Pattern transfer is complicated by the situation where removal of the material adjacent to the spacers also removes a little of the underlying material. This results in higher topography on one side of the spacer than the other.

The positioning of the spacer also depends on the pattern to which the spacer is attached. If the pattern is too wide or too narrow, the spacer position is affected. However, this would not be a concern for critical memory feature fabrication processes which are self-aligned.

Double/Multiple exposure

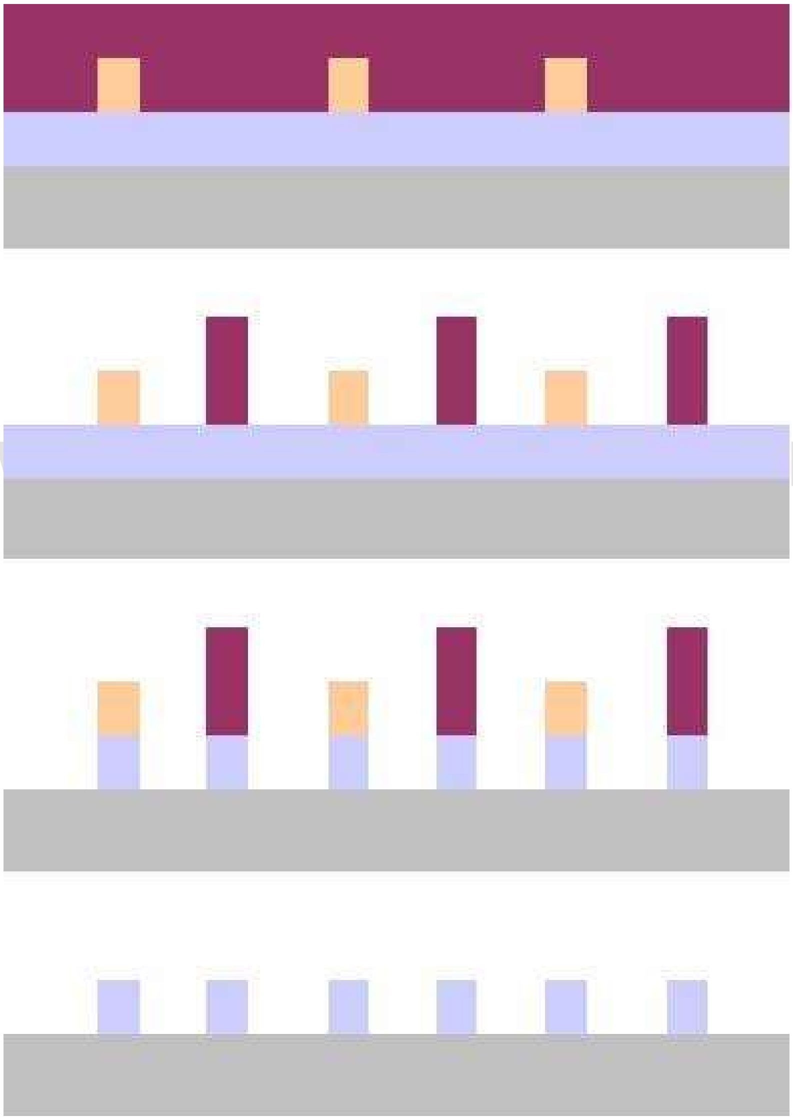


Double exposure: photoresist coating; first exposure; second exposure; development

Double exposure is a sequence of two separate exposures of the same photoresist layer using two different photomasks. This technique is commonly used for patterns in the same layer which look very different or have incompatible densities or pitches. In one important case, the two exposures may each consist of lines which are oriented in one or the other of two usually perpendicular directions. This allows the decomposition of two-dimensional patterns into two one-dimensional patterns which are easier to print. This is the basis of DDL technology from Brion Technologies, a subsidiary of ASML. The sum of the exposures cannot improve the minimum resolution limit unless the photoresist response is not a simple addition of the two exposures. The double exposure technique allows manufacturability of minimum pitch features in a layout that may contain a variety of features. The 65 nm node saw the introduction of alternating phase-shift masks in manufacturing. This technology is typically a double exposure approach. As long as double exposure can be used effectively and is kept within alignment tolerances, it is the preferred patterning approach since it does not require additional follow-up process steps.

Direct-write electron-beam lithography is inherently a multiple exposure technique, as the beam is shaped and projected onto the resist at multiple locations.

Double Expose, Double Etch (mesas)



Double Expose, Double Etch (lines): Photoresist coating over first pattern; photoresist features between previous features; etching; mask removal

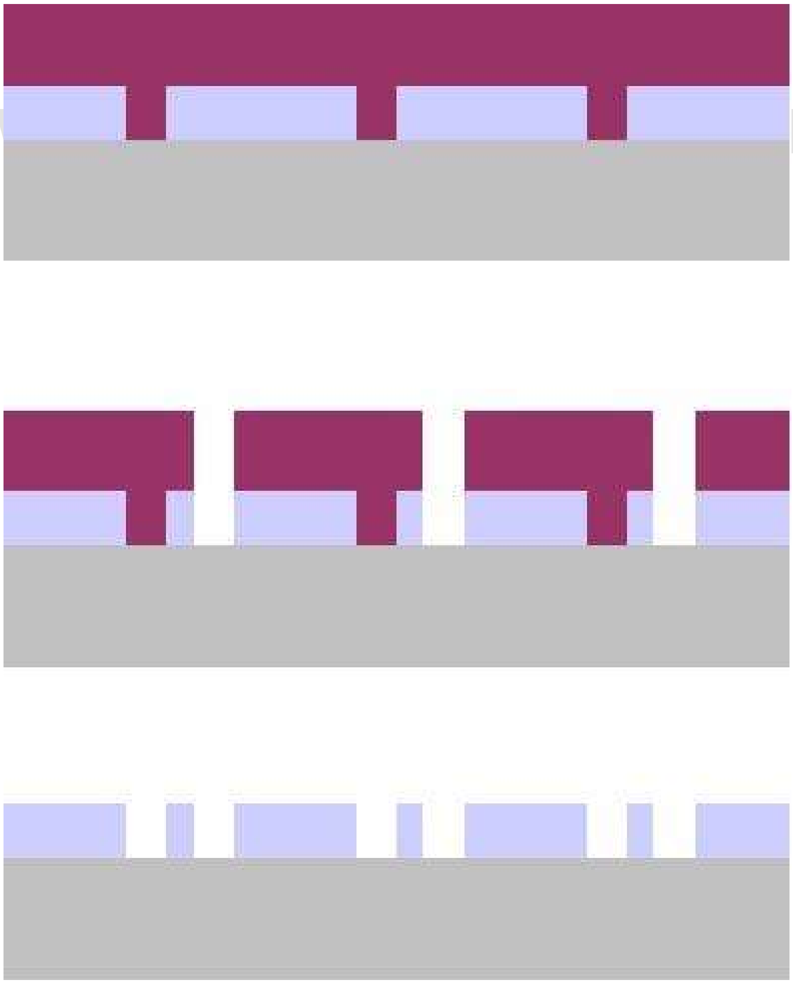
This is best described by considering a process example. A first exposure of photoresist is transferred to an underlying hardmask layer. After the photoresist is removed following the hardmask pattern transfer, a second layer of photoresist is coated onto the sample. This second layer undergoes a second exposure, imaging features in between the features patterned in the hardmask layer. The surface pattern is therefore a set of photoresist features in between hardmask features, which can be transferred into the final layer underneath. This allows a doubling of feature density. The Interuniversity

Microelectronics Centre (IMEC, Belgium) recently used this approach to pattern the gate level for its 32 nm half-pitch demonstration.

A concern with the use of this approach is the discrepancy and delay between the second photoresist pattern and the first hardmask pattern, resulting in an additional source of variation.

A variation on this approach which eliminates the first hardmask etch is resist freezing, which allows a second resist coating over the first developed resist layer. JSR has demonstrated 32 nm lines and spaces using this method, where the freezing is accomplished by surface hardening of the first resist layer.

Double Expose, Double Etch (trenches)



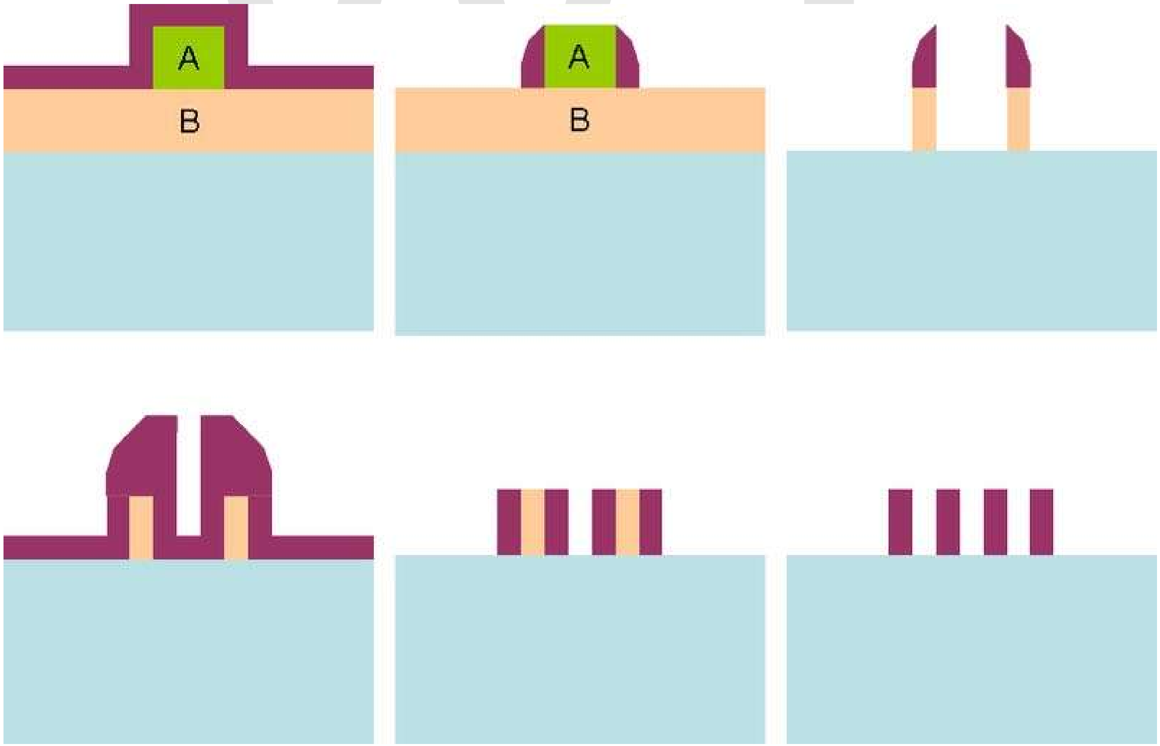
Double Expose, Double Etch (trenches): Photoresist coating over first pattern; etching adjacent to previous features; mask removal

A "brute force" approach for patterning trenches involves a sequence of (at least) two separate exposures and etchings of independent patterns into the same layer. For each exposure, a different photoresist coating is required. When the sequence is completed, the pattern is a composite of the previously etched subpatterns. By interleaving the subpatterns, the pattern density can theoretically be increased indefinitely, the half-pitch being inversely proportional to the number of subpatterns used. For example, a 25 nm half-pitch pattern can be generated from interleaving two 50 nm half-pitch patterns, three 75 nm half-pitch patterns, or four 100 nm half-pitch patterns. The feature size reduction will most likely require the assistance of techniques such as chemical shrinks, thermal reflow, or shrink assist films. This composite pattern can then be transferred down into the final layer.

A possible application would be, for example, dividing the contact layer into two separate groups: gate contacts and source/drain contacts, each defining its own mask. IMEC recently used an approach like this to demonstrate a 45 nm node 6-transistor SRAM cell using dry lithography .

As with the double-expose, double-etch mesas approach, any discrepancy among the different interleaved patterns would be a source of feature-to-feature variation.

Multiple patterning - the ultimate resolution



Feature quadrupling with second spacer patterning: 1st spacer deposition; 1st spacer etch; 1st and 2nd support material etch; 2nd spacer deposition; 2nd spacer etch; 2nd support material etch

The extrapolation of double patterning to multiple patterning has been contemplated, but the issue of cost control is still on the minds of many. While the benefits of multiple patterning in terms of resolution, depth of focus and lithographic defect sensitivity are understood, there is added burden to control the process budget increase and maintain good yield.

Beyond double (2X) patterning, the most frequently published multiple patterning methodology is the repeated spacer approach, which can be practiced in many forms. It is also possible to additively combine two or more of the above approaches. For example, a dual-tone photoresist with pitch-halved acid profile, plus dual-tone development that dissolves the highest and lowest acid concentrations, combined with a spacer process, would result in 8x pitch resolution enhancement,e.g., 40 nm half-pitch reduced to 5 nm half-pitch. Subsequently repeating the spacer process would give 16 x pitch resolution improvement, e.g., 40 nm half-pitch reduced to 2.5 nm half-pitch. The European LENS (Lithography Enhancement Towards Nano Scale) project is targeted toward implementation of both double exposure (resist freezing) and spacer-based process, in principle enabling two ways of patterning for ~20 nm design rules with current lithography tools, already tailored for double patterning or ~10 nm design rules in combination. With successful dual-tone development of a dual-tone photoresist, 2.5 nm design rules can be imagined.

Intel used several spacer deposition/etch/clean steps to demonstrate spacers spaced apart by ~26 nm. It represents a reduction of the original patterned pitch by a factor of ~1/4 and indicates that wavelength and optics no longer purely determine the lithographic resolution.

IMEC has indicated that in the event that EUV lithography is not ready, quadruple patterning (with tighter overlay specifications) would be used.

At the 2010 Flash Memory Summit, it was projected that immersion lithography with multiple patterning would be used to scale NAND Flash to below 20 nm within a few years.

2D layout considerations

For 2D patterns the density increase is very dependent on the nature of the pattern. For instance, contacts arrays have optimal packing density as rectangular arrays for double patterning but as hexagonal close packed arrays for triple patterning - achieving a close to 2 and 3 times area improvement respectively. For 2D layouts double patterning compliance errors occur when there are odd cycles of minimum spaces. This can be resolved by relaxing one of these spaces to a distance where both features can be patterned in the same imaging step. Triple patterning is compliant with odd cycles but in turn is non-complaint for two facing pairs of line-ends where the corner to corner space is below the single patterning distance. This in turn is compliant under quadruple patterning. The improvement in density with the use of multiple patterning schemes is thus highly dependent on the pattern. Often simple redesigns or relaxation of dimensions in one direction can avoid the expense of going to more complex and expensive multiple patterning processes.

Synopsys has begun consideration of triple patterning decomposition of layers which are less easy to split into two patterns, such as contact layers. While only increasing the number of processing steps by 50% (compared to 100% for the insertion of double patterning), triple patterning would enable 16 nm node patterning on a 45 nm node lithography tool. Likewise, quadruple patterning would enable 11 nm node patterning on the same 45 nm node lithography tool, with only 33% additional steps over triple patterning.

Implementations

Due to its rather straightforward application, without the need to change the infrastructure, multiple patterning is not expected to encounter any insurmountable technical or commercialization barriers. Despite the cost and throughput concerns, it has recently received more attention and interest, mainly due to delays in next-generation lithography techniques such as EUVL and nanoimprint lithography.

Multiple patterning can also exploit high-bias processes (for example, photoresist trimming to reduce linewidth, or photoresist reflow to reduce trench width) to substantially eliminate defects sized at around 2x the design pitch or smaller. This is a significant advantage over increasing lithography tool resolution, which exposes the wafer to more defects at the design rule or even smaller.

Electron-beam lithography

As mentioned above, electron-beam lithography is inherently a multiple exposure technique. However, even electron beam lithography would eventually require at least two interleaved exposures (due to secondary electron scattering), for instance, in the fabrication of 15 nm half-pitch X-ray zone plates. In fact, double patterning may not even be sufficient for sub-12 nm half-pitch, even with electron beam lithography. In that case, multiple patterning would be necessary.

Tela Innovations

Tela Innovations, a startup founded in 2005 which has recently garnered significant support and funding, specializes in converting arbitrary layouts into array-like features suitable for double patterning.

Intel

Intel has been using double patterning in its 45 nm as well as its 65 nm technology. Double patterning is used to square off the ends of the transistor gates. The first mask pattern consists of the gate lines linked at the end. The second mask is a line cutter that separates these into separate gates, using a second photoresist coating. The extra steps for the 45 nm double patterning compared to 65 nm are necessary due to the use of dry instead of immersion lithography.

In September 2009, Intel disclosed that for its 15 nm process, EUV did not appear to be ready in timely fashion. Hence, Intel is preparing to extend 193 nm immersion lithography with double and possibly triple patterning to 15 nm.

For 11 nm, Intel expects to be able to use quintuple exposure with 193 nm lithography, where one of the exposures is used with spacer patterning for a further pitch division. The remaining four exposures are for cutting the pitch-divided lines. Even with a next-generation lithography like EUVL or maskless direct-write electron-beam lithography, a second exposure is still required for cutting. Referenced to its 32 nm node technology, the density is expected to be enhanced about 8x (three generations of doubling density), but the cost is less than 6x (5 exposures, with one round of spacer patterning).

NAND Flash Memory Makers

In 2010, IM Flash began producing 25 nm NAND Flash, with the combination of 193 nm immersion lithography and double patterning.

Similar to the multiple patterning approach described for Intel's 11 nm process, in actual practice, NAND Flash memory array patterning using the spacer approach would use 3 or more mask exposures. The first mask patterns the array core by defining the spacers, while a second mask is used to crop or trim the spacers to form individual lines. Lastly, additional masks or multiple patterning would be used to pattern peripheral connections, e.g., pads. As a result, Flash memory patterning can generally be considered multiple patterning, not just a spacer-based double-patterning technique.

Chapter- 3

Electron Beam Lithography

Electron beam lithography (often abbreviated as **e-beam lithography**) is the practice of scanning a beam of electrons in a patterned fashion across a surface covered with a film (called the resist), ("exposing" the resist) and of selectively removing either exposed or non-exposed regions of the resist ("developing"). The purpose, as with photolithography, is to create very small structures in the resist that can subsequently be transferred to the substrate material, often by etching. It was developed for manufacturing integrated circuits, and is also used for creating nanotechnology architectures.

The primary advantage of electron beam lithography is that it is one of the ways to beat the diffraction limit of light and make features in the nanometer regime. This form of maskless lithography has found wide usage in photomask-making used in photolithography, low-volume production of semiconductor components, and research & development.

On the other hand, the key limitation of electron beam lithography is throughput, i.e., the very long time it takes to expose an entire silicon wafer or glass substrate. A long exposure time leaves the user vulnerable to beam drift or instability which may occur during the exposure. Also, the turn-around time for reworking or re-design is lengthened unnecessarily if the pattern is not being changed the second time.

Electron beam lithography systems

Electron beam lithography systems used in commercial applications are dedicated e-beam writing systems that are very expensive (>$4M USD). For research applications, it is very common to convert an electron microscope into an electron beam lithography system using a relatively low cost accessory (<USD 100k). Such converted systems have produced linewidths of ~20 nm since at least 1990, while current dedicated systems have produced linewidths on the order of 10 nm or smaller.

Electron beam lithography systems can be classified according to both beam shape and beam deflection strategy. Older systems used Gaussian-shaped beams and scanned these beams in a raster fashion. Newer systems use shaped beams, which may be deflected to various positions in the writing field (this is also known as **vector scan**).

Electron sources

Lower resolution systems can use thermionic sources, which are usually formed from LaB_6. However, systems with higher resolution requirements need to use field electron emission sources, such as heated W/ZrO_2 for lower energy spread and enhanced brightness. Thermal field emission sources are preferred over cold emission sources, in spite of their slightly larger beam size, because the former offer better stability over typical writing times of several hours.

Lenses

Both electrostatic and magnetic lenses may be used. However, electrostatic lenses have more aberrations and so are not used for fine focusing. There is no current mechanism to make achromatic electron beam lenses, so extremely narrow dispersions of the electron beam energy are needed for finest focusing.

Stage, stitching and alignment

Typically, for very small beam deflections electrostatic deflection 'lenses' are used, larger beam deflections require electromagnetic scanning. Because of the inaccuracy and because of the finite number of steps in the exposure grid the writing field is of the order of 100 micrometre - 1 mm. Larger patterns require stage moves. An accurate stage is critical for stitching (tiling writing fields exactly against each other) and pattern overlay (aligning a pattern to a previously made one).

Electron beam write time

The minimum time to expose a given area for a given dose is given by the following formula:

$$D \cdot A = T \cdot I$$

where T is the time to expose the object (can be divided into exposure time/step size), I is the beam current, D is the dose and A is the area exposed.

For example, assuming an exposure area of 1 cm^2, a dose of 10^{-3} Coulombs/cm^2, and a beam current of 10^{-9} Amperes, the resulting minimum write time would be 10^6 seconds (about 12 days). This minimum write time does not include time for the stage to move back and forth, as well as time for the beam to be blanked (blocked from the wafer during deflection), as well as time for other possible beam corrections and adjustments in the middle of writing. To cover the 700 cm^2 surface area of a 300 mm silicon wafer, the minimum write time would extend to $7*10^8$ seconds, about 22 years. This is a factor of about 10 million times slower than current optical lithography tools. It is clear that throughput is a serious limitation for electron beam lithography, especially when writing dense patterns over a large area.

E-beam lithography is not suitable for high-volume manufacturing because of its limited throughput. The smaller field of electron beam writing makes for very slow pattern generation compared with photolithography (the current standard) because more exposure fields must be scanned to form the final pattern area ($\leq$mm^2 for electron beam vs. $\geq$40 mm^2 for an optical mask projection scanner). The stage moves in between field scans. The electron beam field is small enough that a rastering or serpentine stage motion is needed to pattern a 26 mm X 33 mm area for example, whereas in a photolithography scanner only a one-dimensional motion of a 26 mm X 2 mm slit field would be required.

Currently an optical maskless lithography tool is much faster than an electron beam tool used at the same resolution for photomask patterning.

Defects in electron-beam lithography

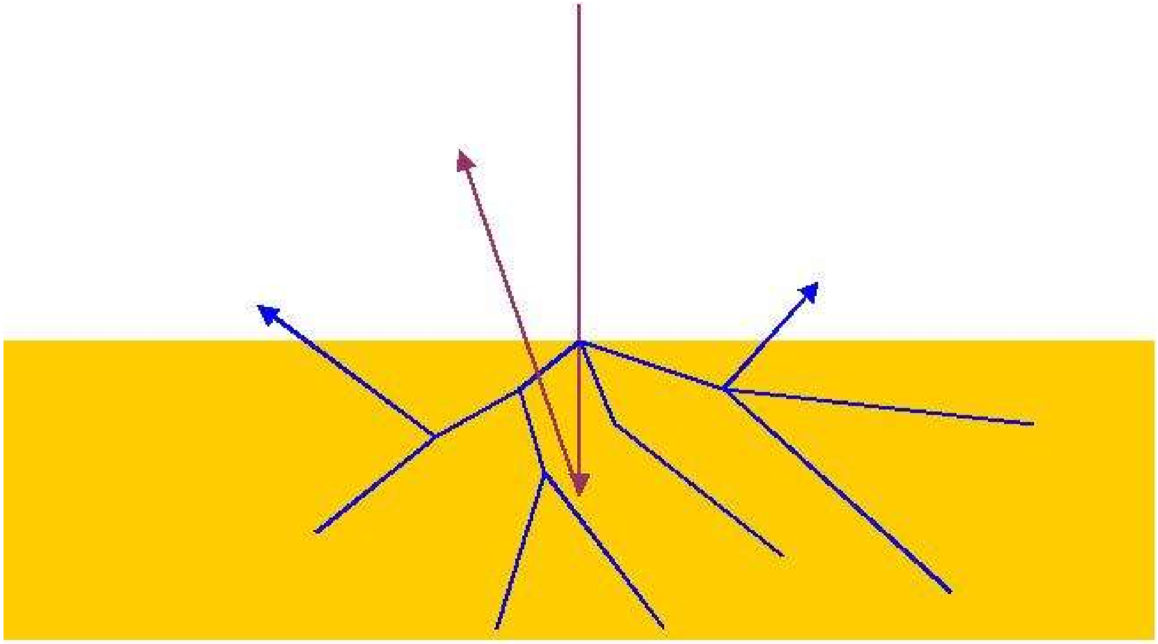
Despite the high resolution of electron-beam lithography, the generation of defects during electron-beam lithography is often not considered by users. Defects may be classified into two categories: data-related defects, and physical defects.

Data-related defects may be classified further into two sub-categories. **Blanking** or **deflection errors** occur when the electron beam is not deflected properly when it is supposed to, while **shaping errors** occur in variable-shaped beam systems when the wrong shape is projected onto the sample. These errors can originate either from the electron optical control hardware or the input data that was taped out. As might be expected, larger data files are more susceptible to data-related defects.

Physical defects are more varied, and can include sample charging (either negative or positive), backscattering calculation errors, dose errors, fogging (long-range reflection of backscattered electrons), outgassing, contamination, beam drift and particles. Since the write time for electron beam lithography can easily exceed a day, "randomly occurring" defects are more likely to occur. Here again, larger data files can present more opportunities for defects.

Photomask defects largely originate during the electron beam lithography used for pattern definition.

Electron energy deposition in matter



Electron trajectories in resist: An incident electron (purple) produces secondary electrons (blue). Sometimes, the incident electron may itself be backscattered as shown here and leave the surface of the resist (amber).

The primary electrons in the incident beam lose energy upon entering a material through inelastic scattering or collisions with other electrons. In such a collision the momentum transfer from the incident electron to an atomic electron can be expressed as $dp = 2e^2 / bv$, where b is the distance of closest approach between the electrons, and v is the incident electron velocity. The energy transferred by the collision is given by $T = (dp)^2 / 2m = e^4 / Eb^2$, where m is the electron mass and E is the incident electron energy, given by $E = (1 / 2)mv^2$. By integrating over all values of T between the lowest binding energy, E_0 and the incident energy, one obtains the result that the total cross section for collision is inversely proportional to the incident energy E, and proportional to $1/E_0 - 1/E$. Generally, $E >> E_0$, so the result is essentially inversely proportional to the binding energy.

By using the same integration approach, but over the range $2E_0$ to E, one obtains by comparing cross-sections that half of the inelastic collisions of the incident electrons produce electrons with kinetic energy greater than E_0. These secondary electrons are capable of breaking bonds (with binding energy E_0) at some distance away from the original collision. Additionally, they can generate additional, lower energy electrons, resulting in an electron cascade. Hence, it is important to recognize the significant contribution of secondary electrons to the spread of the energy deposition.

In general, for a molecule AB:

$$e^- + AB \rightarrow AB^- \rightarrow A + B^-$$

This reaction, also known as "electron attachment" or "dissociative electron attachment" is most likely to occur after the electron has essentially slowed to a halt, since it is easiest to capture at that point. The cross-section for electron attachment is inversely proportional to electron energy at high energies, but approaches a maximum limiting value at zero energy. On the other hand, it is already known that the mean free path at the lowest energies (few to several eV or less, where dissociative attachment is significant) is well over 10 nm, thus limiting the ability to consistently achieve resolution at this scale.

Resolution capability

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 feature resolution limit is determined not by the beam size but by forward scattering (or effective beam broadening) in the photoresist while the pitch resolution limit is determined by secondary electron travel in the photoresist. This point is driven home by the 2007 demonstration of double patterning using electron beam lithography in the fabrication of 15 nm half-pitch zone plates. Although a 15 nm feature was resolved, a 30 nm pitch was still difficult to do, due to secondary electrons scattering from the adjacent feature. The use of double patterning allowed the spacing between features to be wide enough for the secondary electron scattering to be significantly reduced. The forward scattering can be decreased by using higher energy electrons or thinner photoresist, but the generation of secondary electrons is inevitable. It is now recognized that for insulating materials like PMMA, low energy electrons can travel quite a far distance (several nm is possible). This is due to the fact that below the ionization potential the only energy loss mechanism is mainly through phonons and polarons, although the latter is basically an ionic lattice effect. In fact, polaron hopping could extend as far as 20 nm. 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.

Scattering

In addition to producing 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. For thicker electrons, as the primary electrons move forward, they have an increasing opportunity to scatter laterally from the beam-defined location. This scattering is called **forward scattering**. Sometimes the primary electrons are scattered at angles exceeding 90 degrees, i.e., they no longer advance further into the resist. 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 exposure of resist over an area much larger than defined by the beam spot.

Proximity effect

The smallest features produced by electron beam lithography have generally been isolated features, as nested features exacerbate the proximity effect, whereby electrons from exposure of an adjacent region 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. In actuality, though, the range of secondary electron scattering is quite far, sometimes exceeding 100 nm, but becoming very significant below 30 nm.

The proximity effect is also manifest by secondary electrons leaving the top surface of the resist and then returning some tens of nanometers distance away.

Proximity effects (due to electron scattering) can be addressed by solving the inverse problem and calculating the exposure function $E(x,y)$ that leads to a dose distribution as close as possible to the desired dose $D(x,y)$ when convolved by the scattering distribution point spread function $PSF(x,y)$. However, it must be remembered that an error in the applied dose (e.g., from shot noise) would cause the proximity effect correction to fail.

Charging

Since electrons are charged particles, they tend to charge the substrate negatively unless they can quickly gain access to a path to ground. For a high-energy beam incident on a silicon wafer, virtually all the electrons stop in the wafer where they can follow a path to ground. However, for a quartz substrate such as a photomask, the embedded electrons will take a much longer time to move to ground. Often the negative charge acquired by a substrate can be compensated or even exceeded by a positive charge on the surface due to secondary electron emission into the vacuum. The presence of a thin conducting layer above or below the resist is generally of limited use for high energy (50 keV or more) electron beams, since most electrons pass through the layer into the substrate. The charge dissipation layer is generally useful only around or below 10 keV, since the resist is thinner and most of the electrons either stop in the resist or close to the conducting layer. However, they are of limited use due to their high sheet resistance, which can lead to ineffective grounding.

The range of low-energy secondary electrons (the largest component of the free electron population in the resist-substrate system) which can contribute to charging is not a fixed number but can vary from 0 to as high as 50 nm. Hence, resist-substrate charging is not repeatable and is difficult to compensate consistently. Negative charging deflects the electron beam away from the charged area while positive charging deflects the electron beam toward the charged area.

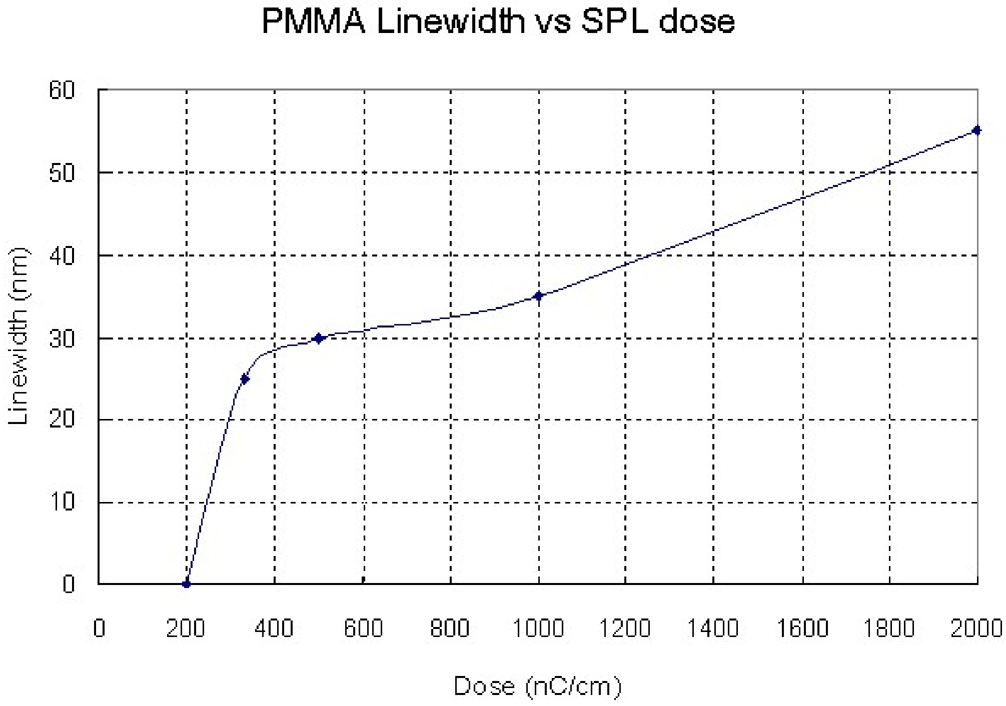
Electron beam resist performance

A study performed at the Naval Research Laboratory indicated that low-energy (10−50 eV) electrons were able to damage ~30 nm thick PMMA films. The damage was manifest as a loss of material.

- For the popular electron-beam resist ZEP-520, a pitch resolution limit of 60 nm (30 nm lines and spaces), independent of thickness and beam energy, was found.
- A 20 nm resolution had also been demonstrated using a 3 nm 100 keV electron beam and PMMA resist. 20 nm unexposed gaps between exposed lines showed inadvertent exposure by secondary electrons.
- Hydrogen silsesquioxane (HSQ) is a negative resist that is capable of forming sub-30 nm lines in very thin layers, but is itself similar to porous, hydrogenated SiO2. It may be used to etch silicon but not silicon dioxide or other similar dielectrics.

New frontiers in electron-beam lithography

To get around the secondary electron generation, it will be imperative to use low-energy electrons as the primary radiation to expose photoresist. Ideally, these electrons should have energies on the order of not much more than several eV in order to expose the photoresist without generating any secondary electrons, since they will not have sufficient excess energy. Such exposure has been demonstrated using a scanning tunneling microscope as the electron beam source. The data suggest that electrons with energies as low as 12 eV can penetrate 50 nm thick polymer photoresist. The drawback to using low energy electrons is that it is hard to prevent spreading of the electron beam in the photoresist. Low energy electron optical systems are also hard to design for high resolution. Coulomb inter-electron repulsion always becomes more severe for lower electron energy.



Scanning probe lithography. A scanning probe can be used for low-energy electron beam lithography, offering sub-100 nm resolution, determined by the dose of low-energy electrons.

Another alternative in electron-beam lithography is to use extremely high electron energies (at least 100 keV) to essentially "drill" or sputter the material. This phenomenon has been observed frequently in transmission electron microscopy. However, this is a very inefficient process, due to the inefficient transfer of momentum from the electron beam to the material. As a result it is a slow process, requiring much longer exposure times than conventional electron beam lithography. Also high energy beams always bring up the concern of substrate damage.

Interference lithography using electron beams is another possible path for patterning arrays with nanometer-scale periods. A key advantage of using electrons over photons in interferometry is the much shorter wavelength for the same energy.

Despite the various intricacies and subtleties of electron beam lithography at different energies, it remains the most practical way to concentrate the most energy into the smallest area.

There has been significant interest in the development of multiple electron beam approaches to lithography in order to increase throughput. This work has been supported by SEMATECH and start-up companies such as Multibeam Corporation and Mapper. However, the degree of parallelism required to be competitive would need to be very high (at least 10 million, as estimated above); this is far in excess of most scheduled demonstrations.

Chapter- 4

Extreme Ultraviolet Lithography

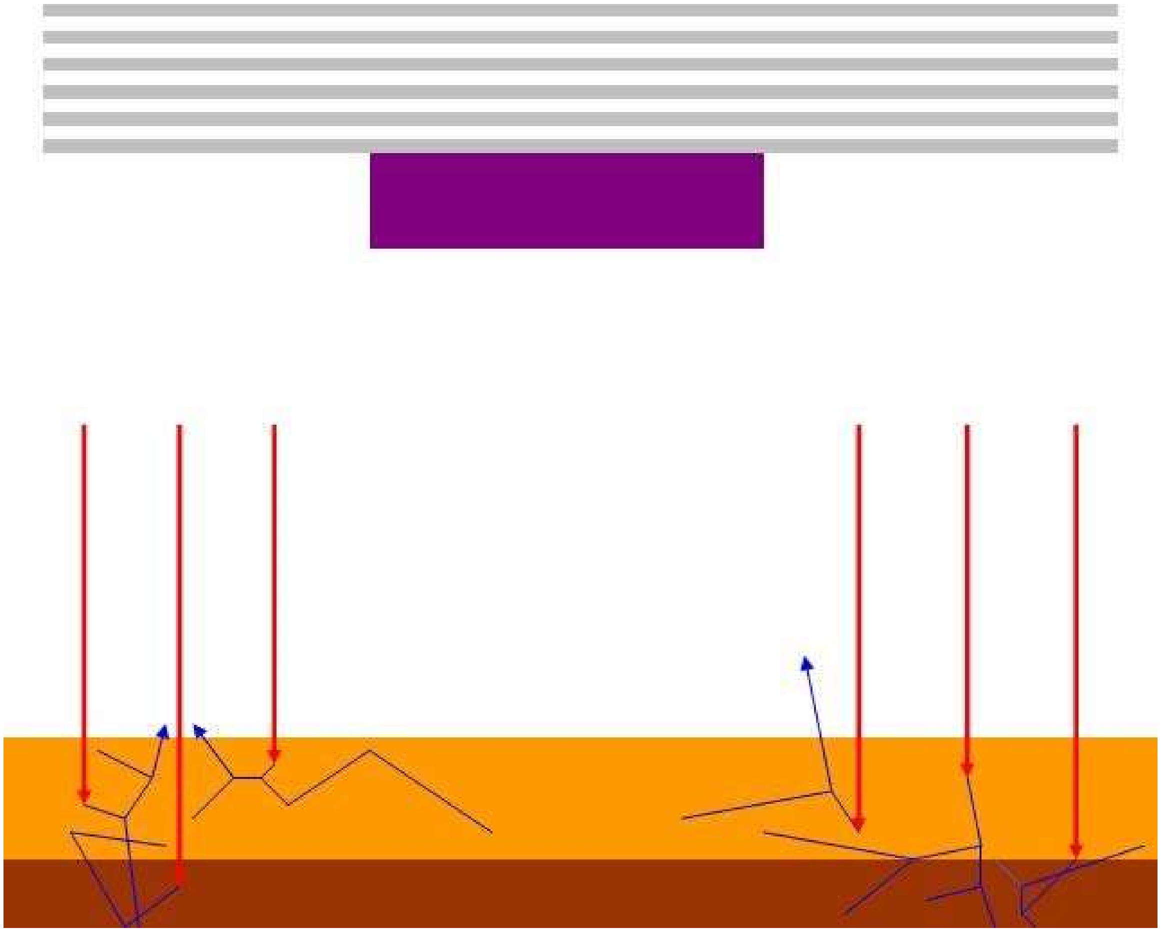


Image formation mechanism in EUV lithography. *Top:* EUV multilayer and absorber (purple) constituting mask pattern for imaging a line. *Bottom:* EUV radiation (red) reflected from the mask pattern is absorbed in the resist (amber) and substrate (brown), producing photoelectrons and secondary electrons (blue). These electrons increase the extent of chemical reactions in the resist. A secondary electron pattern that is random in nature is superimposed on the optical image. The unwanted secondary electron exposure results in loss of resolution, observable line edge roughness and linewidth variation.

Extreme ultraviolet lithography (also known as *EUV* or *EUVL*) is a next-generation lithography technology using an EUV wavelength, currently expected to be 13.5 nm.

EUVL light source

Neutral atoms or condensed matter cannot emit EUV radiation. Ionization must take place first. EUV light can only be emitted by electrons which are bound to multicharged positive ions; for example, to remove an electron from a +3 charged carbon ion (three electrons already removed) requires about 65 eV. Such electrons are more tightly bound than typical valence electrons. The existence of multicharged positive ions is only possible in a hot dense plasma. The Xe or Sn plasma sources for EUV lithography are either discharge-produced or laser-produced. Power output exceeding 100 W is a requirement for sufficient throughput. While state-of-the-art 193 nm excimer lasers offer intensities of 200 W/cm^2, lasers for producing EUV-generating plasmas need to be much more intense, on the order of 10^{11} W/cm^2. This indicates the enormous energy burden imposed by switching from generating 193 nm light (laser output approaching 100 W) to generating EUV light (required laser or equivalent power source output exceeding 10 kW).

A further characteristic of the plasma-based EUV sources under development is that they are not even partially coherent, unlike the KrF and ArF excimer lasers used for current optical lithography. Further power reduction (energy loss) is expected in converting incoherent sources (emitting in all possible directions at many independent wavelengths) to partially coherent (emitting in a limited range of directions within a narrow band of wavelengths) sources by filtering (unwanted wavelengths and directions). On the other hand, coherent light poses a risk of monochromatic reflection interference and mismatch of multilayer reflectance bandwidth.

As of 2008, the development tools had a throughput of 4 wafers per hour with a 120 W source. For a 100 WPH requirement, therefore, a 3 kW source would be needed, which is not available in the foreseeable future. However, EUV photon count is determined by the number of electrons generated per photon which are collected by a photodiode; since this is essentially the highly variable secondary yield of the initial photoelectron, the dose measurement will be impacted by high variability. In fact, data by Gullikson *et al.* indicated ~10% natural variation of the photocurrent responsivity. More recent data for silicon photodiodes remain consistent with this assessment. Calibration of the EUV dosimeter is a nontrivial unsolved issue. **The secondary electron number variability is the well-known root cause of noise in avalanche photodiodes.**

EUVL optics

EUVL is a significant departure from the deep ultraviolet lithography used today. All matter absorbs EUV radiation. Hence, EUV lithography needs to take place in a vacuum. All the optical elements, including the photomask, must make use of defect-free Mo/Si multilayers which act to reflect light by means of interlayer interference; any one of these mirrors will absorb around 30% of the incident light. This limitation can be avoided in maskless interference lithography systems. However, the latter tools are restricted to producing periodic patterns only.

The pre-production EUVL systems built to date contain at least two condenser multilayer mirrors, six projection multilayer mirrors, and a multilayer object (mask). Since the optics already absorbs 96% of the available EUV light, the ideal EUV source will need to be sufficiently bright. EUV source development has focused on plasmas generated by laser or discharge pulses. The mirror responsible for collecting the light is directly exposed to the plasma and is therefore vulnerable to damage from the high-energy ions and other debris. This damage associated with the high-energy process of generating EUV radiation has precluded the successful implementation of practical EUV light sources for lithography.

The wafer throughput of an EUVL exposure tool is a critical metric for manufacturing capacity. Given that EUV is a technology requiring high vacuum, the throughput is limited (aside from the source power) by the transfer of wafers into and out of the tool chamber, to a few wafers per hour.

Another aspect of the pre-production EUVL tools is the off-axis illumination (at an angle of 6 degrees) on a multilayer mask. The resulting asymmetry in the diffraction pattern causes shadowing effects which degrade the pattern fidelity.

EUVL's shorter wavelength also increases flare, resulting in less than perfect image quality and increased line width roughness.

Heating per feature volume (e.g., 20 nm cube) is higher per EUV photon compared to a DUV photon, due to higher absorption in resist. In addition, EUV lithography results in more heating due to the vacuum environment, in contrast to the water cooling environment of immersion lithography.

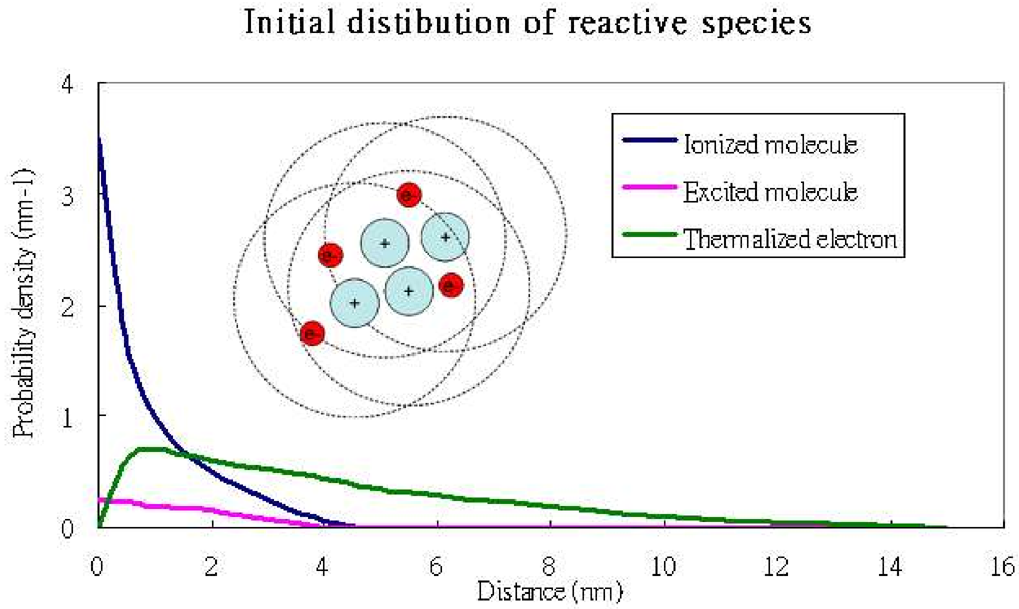
Heating is also a particularly serious issue for multilayer mirrors used, because EUV is absorbed within a thin distance from the surface. The heating density is higher. As a result, water cooling is expected to be used for the high heating load; however, the resulting vibration is a concern.

A recent study by NIST and Rutgers University found that multilayer optics contamination was highly affected by the resonant structure of the EUV mirror influencing the photoelectron generation and secondary electron yield.

Since EUV is highly absorbed by all materials, even EUV optical components inside the lithography tool are susceptible to damage, mainly manifest as observable ablation. Such damage is a new concern specific to EUV lithography, as conventional optical lithography systems use mainly transmissive components and electron beam lithography systems do not put any component in the way of electrons, although these electrons end up depositing energy in the exposed sample substrate.

EUV exposure of photoresist

When an EUV photon is absorbed, photoelectrons and secondary electrons are generated by ionization, much like what happens when X-rays or electron beams are absorbed by matter. It has been estimated that about 4 secondary electrons on average are generated for every EUV photon, although the generation volume is not definite. These secondary electrons have energies of a few to tens of eV and travel tens of nanometers inside photoresist (see below) before initiating the desired chemical reaction. This is very similar to the photoelectron migration for the latent image formation in silver halide photographic films. A contributing factor for this rather large distance is the fact that polymers have significant amounts of free volume. In a recent actual EUV print test, it was found 30 nm spaces could not be resolved, even though the optical resolution and the photoresist composition were not the limiting factor.



Initial distribution of reactive species after EUV absorption. Molecules are excited and ionized within a few nanometers from the absorption point, and electrons are thermalized within 20 nanometers from the absorption point. The inset picture shows the multispur effect, where several electron-ion pairs generated by the EUV photon may interact with one another.

In particular, for photoresists utilizing chemical amplification for higher throughput:

e^- `+ acid generator -> anion -> dissociated anion products`

This reaction, also known as "electron attachment" or "dissociative electron attachment" is most likely to occur after the electron has essentially slowed to a halt, since it is easiest to capture at that point. The cross-section for electron attachment is inversely proportional to electron energy at high energies, but approaches a maximum limiting value at zero energy. On the other hand, it is already known that the mean free path at the lowest energies (few to several eV or less, where dissociative attachment is significant) is well over 10 nm, thus limiting the ability to consistently achieve resolution at this scale.

EUV photoresist images often require resist thicknesses roughly equal to the pitch. This is not only due to EUV absorption causing less light to reach the bottom of the resist but also to forward scattering from the secondary electrons (similar to low-energy electron beam lithography). Conversely, thinner resist transmits a larger fraction of incident light allowing damage to underlying films, yet requires more dosage to achieve the same level of absorption.

Since the photon absorption depth exceeds the electron escape depth, as the released electrons eventually slow down, they dissipate their energy ultimately as heat.

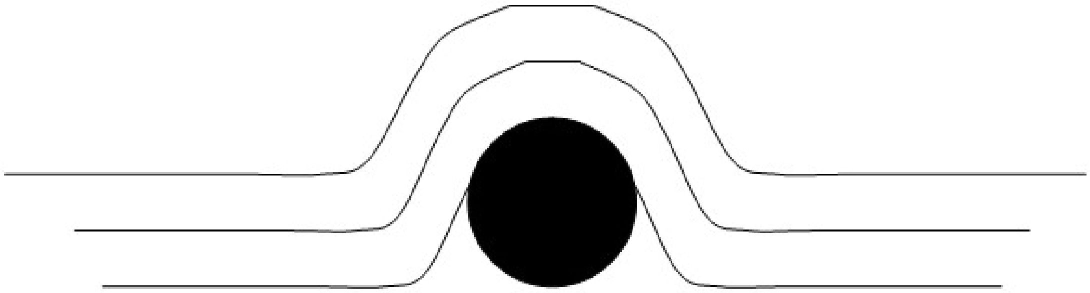
An EUV dose of 1 mJ/cm^2 generates an equivalent photoelectron dose of 10.9 μC/cm^2. Current demonstration doses exceed 10 mJ/cm^2, or equivalently, 109 μC/cm^2 photoelectron dose.

The use of higher doses and/or reduced resist thicknesses to produce smaller features only results in increased irradiation of the layer underneath the photoresist. This adds another significant source of photoelectrons and secondary electrons which effectively reduce the image contrast. In addition, there is increased possibility of ionizing radiation damage to the layers below.

The extent of secondary electron and photoelectrons in blurring the resolution is dependent on factors such as dose, surface contamination, temperature, etc.

EUVL Defects

EUVL faces specific defect issues analogous to those being encountered by immersion lithography. Whereas the immersion-specific defects are due to unoptimized contact between the water and the photoresist, EUV-related defects are attributed to the inherently ionizing energy of EUV radiation. The first issue is positive charging, due to ejection of photoelectrons freed from the top resist surface by the EUV radiation. This could lead to electrostatic discharge or particle contamination as well as the device damage mentioned above. A second issue is contamination deposition on the resist from ambient or outgassed hydrocarbons, which results from EUV- or electron-driven reactions. A third issue is etching of the resist by oxygen, argon or other ambient gases, which have been dissociated by the EUV radiation or the electrons generated by EUV. Ambient gases in the lithography chamber may be used for purging and contamination reduction. These gases are ionized by EUV radiation, leading to plasma generation in the vicinity of exposed surfaces, resulting in damage to the multilayer optics and inadvertent exposure of the sample.



Buried defect on EUV mask blank. A particle on the substrate distorts the multilayer deposited over it, the distortion becoming wider as more layers are added.

Of course mask defects are also a known source of defects for EUVL. The mask defects comprise multilayer defects and defects buried under the multilayer as well as pattern defects. The buried defects are particularly insidious, and even 10 nm defects may be considered risky. The phase shift caused by an undetected 3 nm mask substrate flatness variation is sufficient to produce a printable defect. The principle behind this is a quarter-wavelength deviation from the flat surface produces a half-wavelength optical path difference after reflection. The light that is reflected from the flat surface is 180 degrees out of phase with the light reflected from the quarter-wavelength deviation. It has been shown that even a 1 nm deviation from flatness would lead to a substantial reduction (~20%) of the image intensity. In fact, defects of atomic scale height (0.3-0.5 nm) with 100 nm FWHM can still be printable by exhibiting 10% CD impact. Like a lens, any defect which effectively produces a phase shift scatters light outside the defect region. The amount of light that is scattered can be calculated. Furthermore, the edge of a phase defect will further reduce reflectivity by more than 10% if its deviation from flatness exceeds 3 degrees, due to the deviation from the target angle of incidence of 84 degrees with respect to the surface. Even if the defect height is shallow, the edge still deforms the overlying multilayer, producing an extended region where the multilayer is sloped. The more abrupt the deformation, the narrower the defect edge extension, the greater the loss in reflectivity.

Unexpected Resolution Limits

Given that EUV is a significant reduction in wavelength compared to current lithography wavelengths, one would expect significantly better resolution. However, the resolution is ultimately determined by the interaction volume in the image recording medium, i.e., the photoresist. As noted above, the low energy electrons released by EUV could blur the original EUV image. In addition, there are statistical effects, especially for feature areas less than 1500 square nanometers.

Resist Polymer Aggregates

Resists as polymers are well-known to have aggregates with sizes up to 80 nm. Even the high-resolution resist HSQ has aggregate size reduced down to only 15-20 nm. While the roughness of lines larger than the aggregate size are mildly affected by the aggregate size, below the aggregate size obviously the linewidth can be severely affected.

Shot noise

The required dose sensitivity of 5 mJ/cm^2 implies only several thousand EUV photons or so accumulate in such a small area. With the natural Poisson distribution due to the random arrival times of the photons, there is an expected natural dose variation of at least a few percent 3 sigma, making the exposure process fundamentally uncontrollable for features less than about 40 nm. Increasing the dose will reduce the shot noise, but will also increase the flare dose and generate more free electrons. The free electrons will spread out before slowing to a stop. Since the free electron density is lower than the initial photon density, the shot noise is always effectively larger than expected from just considering the EUV dose.

Intel recently calculated that for printing one billion 30 nm contacts, +/- 16% dose error (@10 mJ/cm^2) is expected from the EUV shot noise. With acid counting, the fluctuation increases to +/- 20%. This issue will affect 22 nm patterning integration. When one considers that within a 1 nm pixel, the shot noise is even more significant (>100% on 10 nm scale @10 mJ/cm^2), the origin of the line edge roughness (LER) issue in EUV lithography becomes clearer.

The 2D patterns often encountered in DRAM and logic microprocessors (including multiple pattern cutting for 11 nm node) as well as the floating gate Flash memory patterns with 2D isolation for charge trapping are more susceptible to shot noise than line-type features. It is because the 2D pattern (ideally rectangular) is defined by the number of photons in a limited area exposed above or below a certain threshold dose.

Dose (mJ/cm^2)	**Photons/nm^2**	**No. of photons in 25 nm diameter**	**6s/avg dose noise (30% absorbed)**
5	3.4	1667	26.8%
10	6.8	3335	19.0%
15	10.2	5002	15.5%
20	13.6	6669	13.4%

25	17.0	8337	12.0%

Note: 1-10 ppb of population is about 6 standard deviations away from the mean dose.

Ref.: EUV resist TWG 2008

The shot noise issue is also applicable to the features patterned on masks used for EUV, targeted at 20 nm and below. A 12 uC/cm^2 absorbed dose used to pattern 80 nm contact holes on a mask (to print 20 nm on wafer) inevitably experiences 10% shot noise in the dose level over the population of a billion such contact holes.

Proximity effect (secondary electrons)

It is now recognized that for insulating materials like PMMA, low energy electrons can travel quite a far distance (several nm is possible). This is due to the fact that below the ionization potential the only energy loss mechanism is mainly through phonons and polarons. It should be noted that polaronic effects are manifest more strongly in ionic crystals than polymers. In fact, polaron hopping could extend as far as 20 nm.

Adding a worst case of ~20 nm broadening to an expected EUV tool resolution of ~ 10 nm, we expect the practical effective resolution to be at best ~30 nm, which is comparable to state-of-the-art immersion lithography with current double patterning lithography. Allowing 20 nm electron range to be only 10% of the critical dimension as variability, automatically challenges sub-200 nm lithography.

In a classic experiment by Feder et al. at IBM, an erbium layer on a PMMA resist layer was exposed to X-rays. The erbium layer absorbed the X-rays strongly, producing low energy secondary electrons. The X-rays which were not absorbed continued to penetrate into the PMMA, where they were only lightly absorbed. Upon removal of the erbium layer and subsequent PMMA development in solvent, the resist removal rate was found to be accelerated for the top 40 nm of the PMMA film, while it was much more gradual for the rest of the film. The accelerated rate was due to the secondary electron exposure, while the gradual rate was due to the X-ray absorption. This proved the maximum secondary electron exposure range of 40 nm in this case.

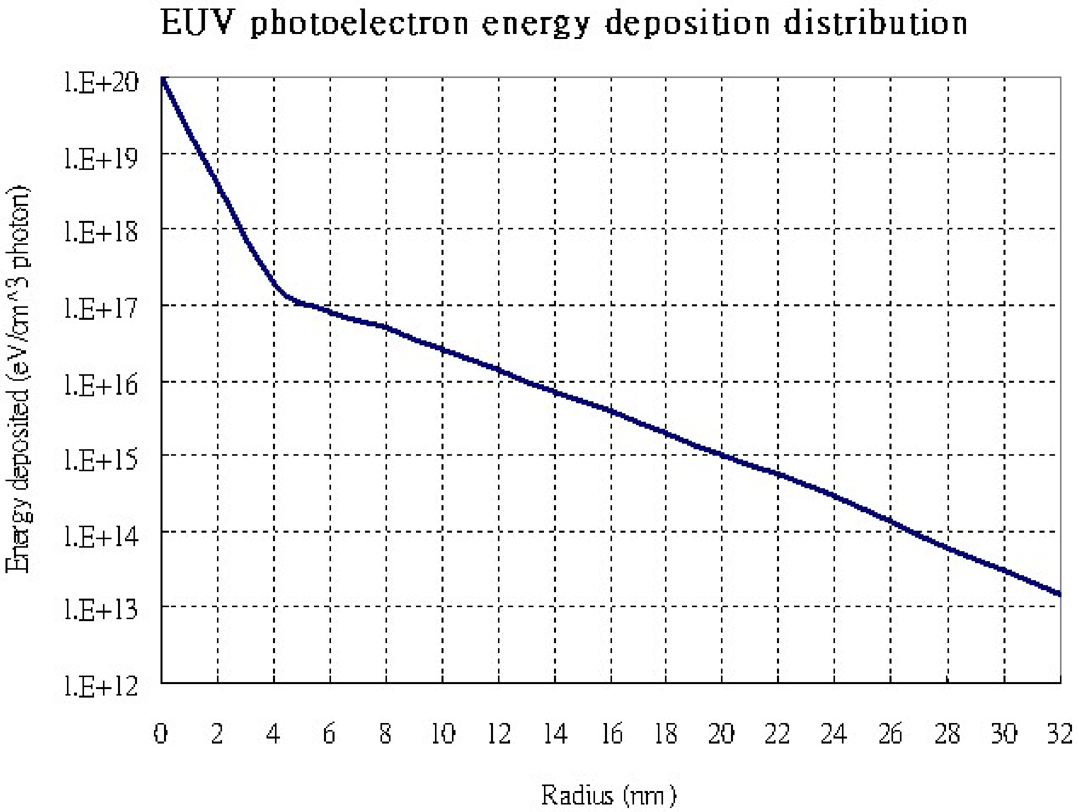
A more recent experiment was performed by Carter et al. at MIT and University of Wisconsin–Madison, where the X-ray absorber generating the electrons was beneath the PMMA resist rather than on top of it. In this case, the accelerated dissolution of PMMA started approximately 50 nm above the substrate.

The significance of this secondary electron range is the appearance of a "proximity effect" for distances on the order of 50 nm or less. This causes the exposure tolerance to be reduced dramatically as feature sizes decrease below this range. Even though features can still print below this range, the resolution is affected by the randomness of energy distribution. The difference in experimentally determined ranges above (40 nm vs. 50 nm) is an indication of this fundamental variability. The secondary electron exposure can also be thought of as a blur effect. The blur is generally not included in optical-only image simulations.

The proximity effect is also manifest by photoelectrons and secondary electrons leaving the top surface of the resist and then returning some tens of nanometers distance away. This also can be understood in terms of the emitted electrons forming a space charge cloud above the surface which is attracted to the positively charged surface in the vertical direction but laterally disperses (in vacuum) due to the negative charge mutual repulsion.

The secondary electron proximity effect was recently demonstrated by Stanford University using a scanning probe tip that emitted electrons in the 40-60 eV energy range. Dose sensitivity was demonstrated more than 25 nm away from the exposure center. It indicates that within a 50 nm range of exposure widths, the low-energy (EUV-generated) electron distribution influences the linewidth distribution. This is a new effect not seen with conventional optical lithography.

Photoelectron trajectories



Radial energy distribution from EUV photoelectrons. For photons incident at r=0, the radial range can be as large as 30 nm, but the highest amount of energy is deposited within a few nm distance. By adding up the radial energy distributions from many photons incident at different locations within a target area, the amount of deposited energy accumulates, enabling effects at further distances from the target area.

Kotera et al. performed EUV photoelectron trajectory simulations, showing their range to be 30 nm. The spread of the energy deposition by these electrons can account for the observed line edge roughness. The top layer exposure is effectively less because electrons emitted from the surface never come back.

Efficient photoresist heating

Ritucci et al., reported on the improved thermal ablation efficiency for EUV wavelengths compared to DUV wavelengths. Since EUV exceeds the bandgap of all materials, it is more easily absorbed than longer wavelengths, and the same dose of incident energy results in more heating; even ~100 mJ/cm^2 would be hot enough to result in ablation. The resolution of chemically amplified photoresists is determined by thermally driven acid diffusion (spreading). It is worth noting that even at the ablation dose of 100 mJ/cm^2, the shot noise for a 1 nm pixel is still significant (3σ/avg = 36%), which could severely impact a critical dimension (CD) for which the pixel is at least 5%, i.e., 20 nm or less.

Point spread function of resist

Kozawa et al. determined the point spread function of EUV chemically amplified resists using a basic acid generation calculation and simulation fit. The range of acid generation extended ~20 nm from the absorption point, entailing a ~40 nm resolution limit.

Given that photoresists easily diffuse acid molecules, it would be no surprise that the smaller and lighter electrons produced by EUV or other ionizing radiation would diffuse faster and further, rendering the expected optical resolution meaningless.

The resist blur based on print results at the end of 2008 is in the range of 10-16 nm. Half-pitch resolution is still a struggle below 30 nm, and line edge roughness is still a major issue.

EUVL Demonstrations

Interference lithography at the Paul Scherrer Institute has been used to demonstrate sub-20 nm line-space features. However, it must be kept in mind a range of ultraviolet and X-ray wavelengths corresponding to the photon energy range 10-135 eV are included in the synchrotron light spectrum that is used as the source. The resist performance tested with this source therefore does not reflect the performance expected for an EUV projection tool.

In 1996, a collaboration between Sandia National Laboratories, University of California at Berkeley, and Lucent Technologies, produced NMOS transistors with gate lengths from 75 nm to 180 nm. The gate lengths were defined by EUV lithography . The device saturation current at 130 nm gate length was ~0.2 mA/um. A 100 nm gate device showed subthreshold swing of 90 mV/decade and saturated transconductance of 250 mS/mm. A commercial NMOS at the same design rule patterned by then-state-of-the-art DUV lithography showed 0.94 mA/um saturation current and 860 mS/mm saturated transconductance. The subthreshold swing in this case was less than 90 mV/decade.

In February 2008, a collaboration including IBM and AMD, based at the College of Nanoscale Science and Engineering (CNSE) in Albany, New York, used EUV lithography to pattern 90 nm trenches in the first metal layer of a 45 nm node test chip. No specific details on device performance were given. However, the lithographic performance details given still indicated much to be desired:

- CD uniformity: 6.6%
- Overlay: 17.9 nm x, 15.6 nm y, possibly correctable to 6.7 nm x, 5.9 nm y
- Power: 1 W at wafer (>200 W required for high volume), with a dose of 3.75 mJ/cm^2
- Defects: 1/sq. cm.

The high defect level may not be unexpected as AMD's 45 nm node Metal 1 design rule was 90 nm while the same EUV exposure theoretically could result in printed defects below 30 nm originating from mask defects larger than 100 nm. Optical lithography pushed beyond its natural resolution limit has a significant advantage in this regard.

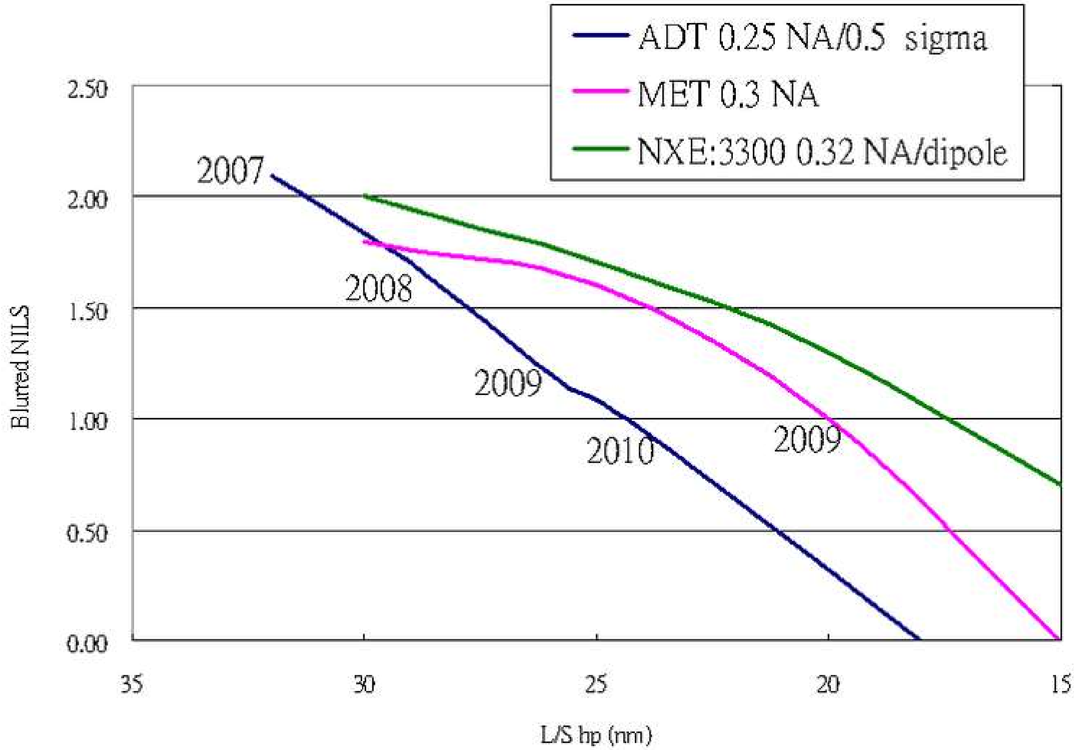
Apparently, the CNSE EUV tool suffered from a well-known 16% flare problem. Flare effects may be difficult to separate from the secondary electron effects discussed earlier.

Also in July 2008, IMEC printed ~60 nm contacts using their installed EUV tool. Doses of 12-18 mJ/cm^2 were used.

In August 2008, SEMATECH demonstrated a 22 nm half-pitch using chemically-amplified photoresist. However, even at 15 mJ/cm^2, the linewidth roughness was very significant, 5-6 nm, so that even the image pitch regularity was challenged.

In April 2009, IMEC fabricated 22 nm SRAM cells where the contact and Metal 1 layers (~45 nm design rule) were printed with EUV lithography. However, it was acknowledged that EUV would not be ready when companies start using 22 nm. In addition, it was commented that the feature edge profiles indicated slope asymmetry related to the characteristic EUV illumination asymmetry. Whereas this demonstration only focused on a limited number of ~45 nm features, Intel's shot noise calculation above for billions of features ~ 30 nm indicates difficult challenges ahead for manufacturing.

In late 2009, KLA-Tencor and GlobalFoundries along with Lawrence Berkeley National Labs published a paper which showed the stochastic behavior of EUV-generated secondary electrons in EUV resists. In particular, 32 nm half-pitch trenches showed significant edge roughness, width roughness and critical dimension (CD) variability. It may also explain the ~ 15 nm resist blur observed in an earlier study.



Trend of demonstrated resolution. Data presented at the International Workshop on EUVL 2010 by ASML indicates difficulty patterning below 32 nm due to NILS decreasing below 2.

Timing impact

"Good progress has been made on all the technology fronts," said Paolo Gargini, Director of Technology Strategy for Intel Corporation. He continued, "Commercialization in 2009 remains the main goal for all the EUV community." However, as of today, EUVL still has not been commercialized.

The difficulties of EUV stem mainly from the difficulty of EUV light generation and the sensitivity of EUV light to surface contamination and roughness.

2009

In July 2009, ASML Holding and Cymer Inc. announced the shipment of the first fully integrated laser-produced plasma (LPP) Extreme Ultraviolet (EUV) lithography light source from Cymer to ASML, where it is supporting integration and testing of next generation EUV lithography scanners.

In July 2009, a review of the EUV infrastructure indicated that there were significant gaps remaining, in particular for mask defect inspection. The gaps may not be filled until

2013 or later, which would impact the rollout of EUV for high-volume manufacturing by 2015.

It was most recently indicated that EUV mask features ~100 nm half-pitch (on the mask itself) were at the current resolution limit of EUV mask generation. Since these features would be demagnified 4X for upcoming 300 mm tools, it would indicate the mask itself would not be able to conventionally print good images at ~25 nm half-pitch or below. The same study reiterated that resolution was not limited by the optics but by the resist response, which prevented sub-20 nm half-pitch even with mask resolution enhancement. This resolution limit on the mask itself could be tied to the shot noise issue pointed out above which is involved in the fabrication of the mask.

2010

In June 2010, TSMC announced it would take delivery of an EUV system for R&D purposes, to be delivered in 2011. The tool's weight reportedly warranted purchasing a special clamp costing more than 2 million USD.

In July 2010, at Semicon West 2010, ASML updated the resolution achieved by EUVL, the status being 24 nm in 2010, but with a severely degraded NILS (normalized image log-slope) below 1.0, indicating poor lithographic quality. In fact, as finer resolution is projected, the NILS is expected to go to 0, indicating impossibility of EUVL use.

In 2010, Samsung cited various additional processes still needed to be developed to address line-width roughness (LWR), arising from the shot noise discussed earlier, which would drive up costs. In addition, it cited out-of-band wavelengths in the DUV range as causing flare effects; this was also observed by others.

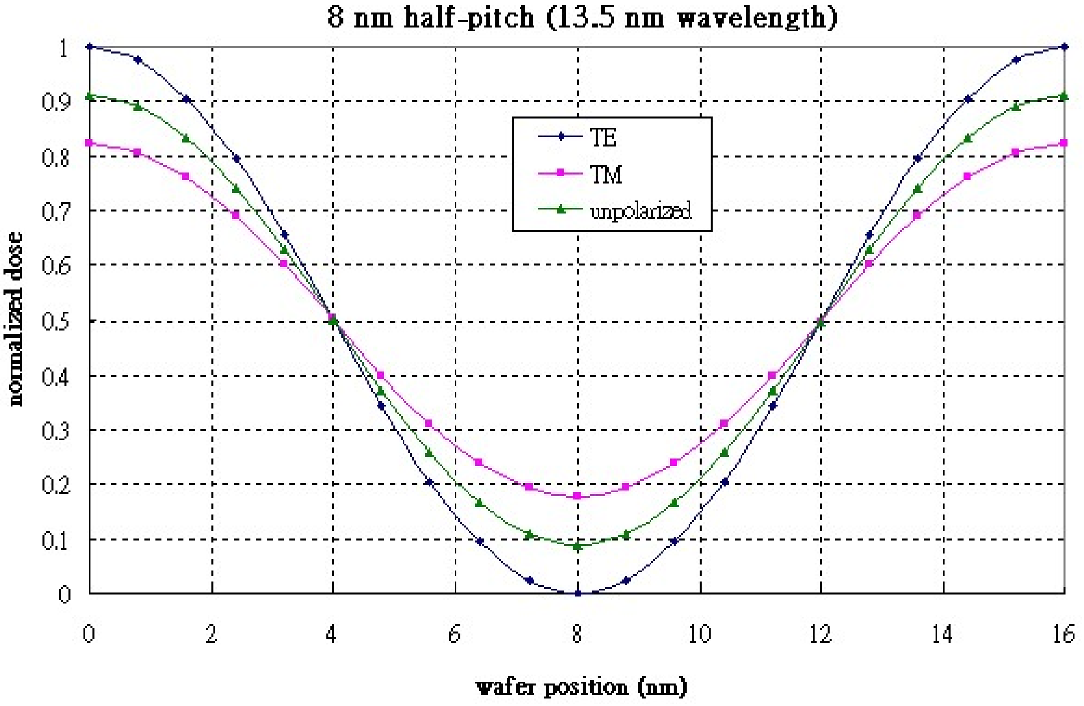
At SPIE 2010, researchers from the Center for X-ray Optics at Lawrence Berkeley National Laboratory and the University of Berkeley presented results showing that replicated surface roughness (RSR) from the substrate to the multilayer surface as low as 50 pm could induce phase errors that are imaged as speckle with defocus, which would lead to line-edge roughness (LER) that could not be tolerated for the 22 nm and 16 nm nodes. This spec is much smaller than current capabilities. For reference, the Bohr radius is 53 pm and the rms surface roughness of silicon wafers is on the order of 100 pm.

ASML EUV tools in use or in development:

Available Year	EUV Tool	Resolution	Throughput	Dose, Source
2006	ADT	32 nm	4 WPH	5 mJ/cm^2, ~8W
2010	NXE:3100	27 nm	60 WPH	10 mJ/cm^2, >100W

2012	NXE:3300B	22 nm	125 WPH	15 mJ/cm^2, >250W
2013	NXE:3300C	Depends on resist diffusion length	150 WPH	15 mJ/cm^2, >350W

Timing for 2x nm and beyond



Polarization effects below 10 nm hp. Below 10 nm, the polarization effects could complicate scaling of EUV lithography. For the most ideal 8 nm half-pitch pattern shown here, the effective flare due to the polarization effect is 18%.

Hynix has found that 193 nm immersion lithography with double patterning could resolve down to ~ 20 nm, while the more cost-conscious EUV approach could only resolve down to 28 nm, less than a generation's improvement over 193 nm immersion lithography single patterning's resolution limit of 38 nm.

Due to its current resolution limitations and lack of readiness, EUVL has recently been supplanted by multiple patterning using existing immersion lithograpy tools as the lithography of choice for current 20-nm class NAND Flash technology generations and beyond. Samsung and IM Flash Technologies have already started using spacer double patterning for their 3X nm NAND Flash.

In September 2009, Intel disclosed that for its 15 nm process, EUV did not appear to be ready in timely fashion. Hence, Intel is preparing to extend 193 nm immersion lithography with double and possibly triple patterning to 15 nm. Currently, it is also exploring the feasibility of EUV for its 11 nm logic node; however, 2D contact patterning still appears only good to ~ 26 nm half-pitch, while a special rinse for improving line width roughness appears very pitch-dependent.

As of 2010, it has been observed that EUV would be delayed until 2015 to allow the development of the required EUV inspection tools. On the other hand, manufacturer roadmaps show 2012-2013 as the timing needed for 1x nm, precluding the use of EUV. Consideration of long-term implementation of EUVL will now need to consider sub-10 nm design rules. However, at this point, due to larger electric field vector angles, polarization effects become important. The effective flare for 10 nm half-pitch lines-spaces due to polarization effects is 11%. The difficulty of EUV is the lack of polarization control (no laser sources, only plasmas).

ASML has indicated that below 16 nm capability would require a larger illumination angle than the current 6°, and hence require a fundamental change to the current EUV multilayer optics infrastructure.

Another issue is that for sub-10 nm applications, the electron beam lithography for EUV mask patterning, already burdened by throughput issues, will have practical resist difficulties for meeting the resolution requirement.

Recent EUV zone plate lithography reports have indicated that for sub-20 nm half-pitch, even next-generation lithography would require double patterning; in fact, double patterning may not be sufficient even for sub-12 nm half-pitch. As a result, the overlay and throughput requirements would need to be at least twice as stringent as before.

Chapter- 5

Nanoimprint Lithography

Nanoimprint lithography is a method of fabricating nanometer scale patterns. It is a simple nanolithography process with low cost, high throughput and high resolution. It creates patterns by mechanical deformation of imprint resist and subsequent processes. The imprint resist is typically a monomer or polymer formulation that is cured by heat or UV light during the imprinting. Adhesion between the resist and the template is controlled to allow proper release.

History

Nanoimprint lithography was first invented by Dr. Bacher and his students. Soon after its invention, many researchers developed many different variations and implementations. At this point, nanoimprint lithography has been added to the International Technology Roadmap for Semiconductors (ITRS) for the 32 and 22 nm nodes.

Processes

There are many different types of nanoimprint lithography, but two of them are most important: thermoplastic nanoimprint lithography and photo nanoimprint lithography.

Thermoplastic nanoimprint lithography

Thermoplastic nanoimprint lithography (T-NIL) is the earliest nanoimprint lithography developed by Dr. Bacher's group. In a standard T-NIL process, a thin layer of imprint resist (thermoplastic polymer) is spin coated onto the sample substrate. Then the mold, which has predefined topological patterns, is brought into contact with the sample and they are pressed together under certain pressure. When heated up above the glass transition temperature of the polymer, the pattern on the mold is pressed into the softened polymer film . After being cooled down, the mold is separated from the sample and the pattern resist is left on the substrate. A pattern transfer process (reactive ion etching, normally) can be used to transfer the pattern in the resist to the underneath substrate.

Photo nanoimprint lithography

In photo nanoimprint lithography (P-NIL), a photo(UV) curable liquid resist is applied to the sample substrate and the mold is normally made of transparent material like fused silica. After the mold and the substrate are pressed together, the resist is cured in UV light and becomes solid. After mold separation, a similar pattern transfer process can be used to transfer the pattern in resist onto the underneath material. The use of a UV-transparent mold is difficult in a vacuum, because a vacuum chuck to hold the mold would not be possible.

Schemes

Full wafer nanoimprint

In a full wafer nanoimprint scheme, all the patterns are contained in a single nanoimprint field and will be transferred in a single imprint step. This allows a high throughput and uniformity. An at least 8-inch (203 mm) diameter full-wafer nanoimprint with high fidelity is possible.

To ensure the pressure and pattern uniformities of full wafer nanoimprint processes and prolong the mold lifetime, a pressing method utilizing isotropic fluid pressure, named Air Cushion Press (ACP) by its inventors, is developed and being used by commercial nanoimprint systems.

Step and repeat nanoimprint

Nanoimprint can be performed in a way similar to the step and repeat optical lithography. The imprint field (die) is typically much smaller than the full wafer nanoimprint field. The die is repeatedly imprinted to the substrate with certain step size. This scheme is good for nanoimprint mold creation. It is currently limited by the throughput, alignment and street width issues.

Applications

Nanoimprint lithography has been used to fabricate devices for electrical, optical, photonic and biological applications. For electronics devices, NIL has been used to fabricate MOSFET, O-TFT, single electron memory. For optics and photonics, intensive study has been conducted in fabrication of subwavelength resonant grating filter, polarizers, waveplate, anti-reflective structures, integrated photonics circuit and plasmontic devices by NIL. sub-10 nm nanofluidic channels had been fabricated using NIL and used in DNA strenching experiment. Currently, NIL is used to shrink the size of biomolecular sorting device an order of magnitude smaller and more efficient.

Benefits

A key benefit of nanoimprint lithography is its sheer simplicity. The single greatest cost associated with chip fabrication is the optical lithography tool used to print the circuit patterns. Optical lithography requires high powered excimer lasers and immense stacks of precision ground lens elements to achieve nanometer scale resolution. There is no need for complex optics or high-energy radiation sources with a nanoimprint tool. There is no need for finely tailored photoresists designed for both resolution and sensitivity at a given wavelength. The simplified requirements of the technology lead to its low cost.

Imprint lithography is inherently a three-dimensional patterning process. Imprint molds can be fabricated with multiple layers of topography stacked vertically. Resulting imprints replicate both layers with a single imprint step, which allows chip manufactures to reduce chip fabrication costs and improve product throughput. As mentioned above, the imprint material does not need to be finely tuned for high resolution and sensitivity. A broader range of materials with varying properties are available for use with imprint lithography. The increased material variability gives chemists the freedom to design new functional materials rather than sacrificial etch resistant polymers. A functional material may be imprinted directly to form a layer in a chip with no need for pattern transfer into underlying materials. The successful implementation of a functional imprint material would result in significant cost reductions and increased throughput by eliminating many difficult chip fabrication processing steps.

Concerns

The key concerns for nanoimprint lithography are overlay, defects, template patterning and template wear. However, recently Kumar et al. have shown that amorphous metals (metallic glasses) can be patterned on sub-100 nm scale, which can significantly reduce the template cost.

Overlay

The current overlay 3 sigma capability is 10 nm. Overlay has a better chance with step-and-scan approaches as opposed to full-wafer imprint.

Defects

As with immersion lithography, defect control is expected to improve as the technology matures. Defects from the template with size below the post-imprint process bias can be eliminated. Other defects would require effective template cleaning and/or the use of intermediate polymer stamps. When vacuum is not used during the imprint process, air can get trapped, resulting in bubble defects. This is because the imprint resist layer and the template or stamp features are not perfectly flat. There is an elevated risk when the intermediate or master stamp contains depressions (which are especially easy air traps), or when the imprint resist is dispensed as droplets just before imprinting, rather than pre-spun onto the substrate. Sufficient time must be allowed for the air to escape.

Template patterning

High resolution template patterning can currently be performed by electron beam lithography or focused ion beam patterning; however at the smallest resolution, the throughput is very slow. As a result, optical patterning tools will be more helpful if they have sufficient resolution. Such an approach has been successfully demonstrated by Greener et al. whereby robust templates were rapidly fabricated by optical patterning of a photoresist-coated metal substrate through a photomask. Other patterning techniques (including even double patterning) may also be used. Kumar and Schroers at Yale developed the nanopatterning of amorphous metals which can be used as inexpensive templates for nanoimprinting.

Template wear

The use of substantial pressure to not only contact but also penetrate a layer during imprinting accelerates the wear of imprint templates compared to other types of lithographic masks.

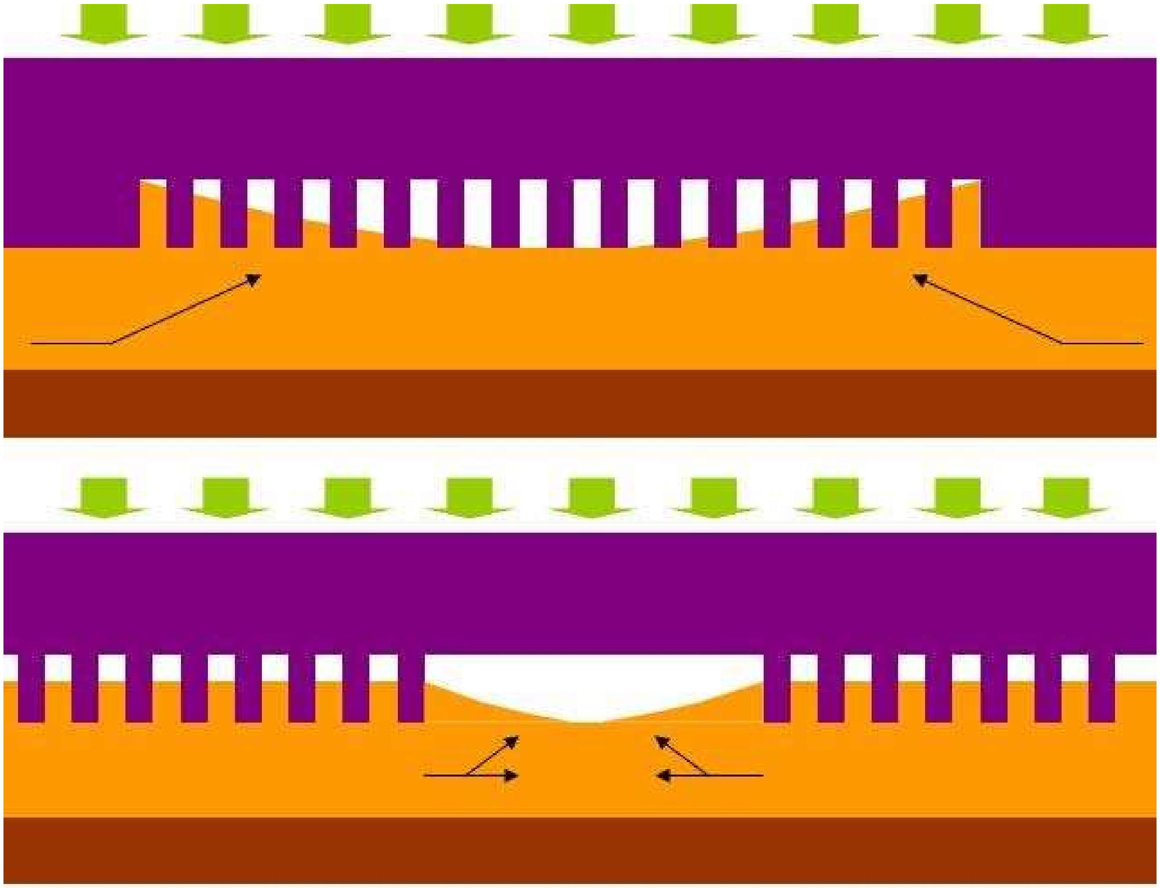
Other

Future applications of nanoimprint lithography may involve the use of porous low-k materials. These materials are not stiff and, as part of the substrate, are readily damaged mechanically by the pressure of the imprint process.

Removal of residual layers

A key characteristic of nanoimprint lithography (except for electrochemical nanoimprinting) is the residual layer following the imprint process. It is preferable to have thick enough residual layers to support alignment and throughput and low defects. However, this renders the nanoimprint lithography step less critical for critical dimension (CD) control than the etch step used to remove the residual layer. Hence, it is important to consider the residual layer removal an integrated part of the overall nanoimprint patterning process. In a sense, the residual layer etch is similar to the develop process in conventional lithography. It has been proposed to combine photolithography and nanoimprint lithography techniques in one step in order to eliminate the residual layer.

Proximity effects



Nanoimprint proximity effect. *Top:* Array of depressions is more quickly filled at the edge than the center, resulting in less imprinting at the center of the array. *Bottom:* The wide space between two groups of protrusions tends to be filled slower than the narrow spaces between the protrusions, resulting in the formation of holes in the unpatterned area.

Nanoimprint lithography relies on displacing polymer. This could lead to systematic effects over long distances. For example, a large, dense array of protrusions will displace significantly more polymer than an isolated protrusion. Depending on the distance of this isolated protrusion from the array, the isolated feature may not imprint correctly due to polymer displacement and thickening. Resist holes can form in between groups of protrusions. Likewise, wider depressions in the template do not fill up with as much polymer as narrower depressions, resulting in misshapen wide lines. In addition, a depression at the edge of a large array fills up much earlier than one located in the center of the array, resulting in within-array uniformity issues.

3D-patterning

A unique benefit of nanoimprint lithography is the ability to pattern 3D structures, such as damascene interconnects and T-gates, in fewer steps than required for conventional lithography. This is achieved by building the T-shape into the protrusion on the template.

Alternative approaches

Electrochemical nanoimprinting

Electrochemical nanoimprinting can be achieved using a stamp made from a superionic conductor such as silver sulfide . When the stamp is contacted with metal, electrochemical etching can be carried out with an applied voltage. The electrochemical reaction generates metal ions which move from the original film into the stamp. Eventually all the metal is removed and the complementary stamp pattern is transferred to the remaining metal.

Laser assisted direct imprint

Laser assisted direct imprint (LADI) is a rapid technique for patterning nanostructures in solid substrates and it does not require etching. A single or multiple excimer laser pulses melt a thin surface layer of substrate material, and a mold is embossed into the resulting liquid layer. A variety of structures with resolution better than 10 nm have been imprinted into silicon using LADI, and the embossing time is less than 250 ns. The high resolution and speed of LADI, attributed to molten silicon's low viscosity (one-third that of water), could open up a variety of applications and be extended to other materials and processing techniques.

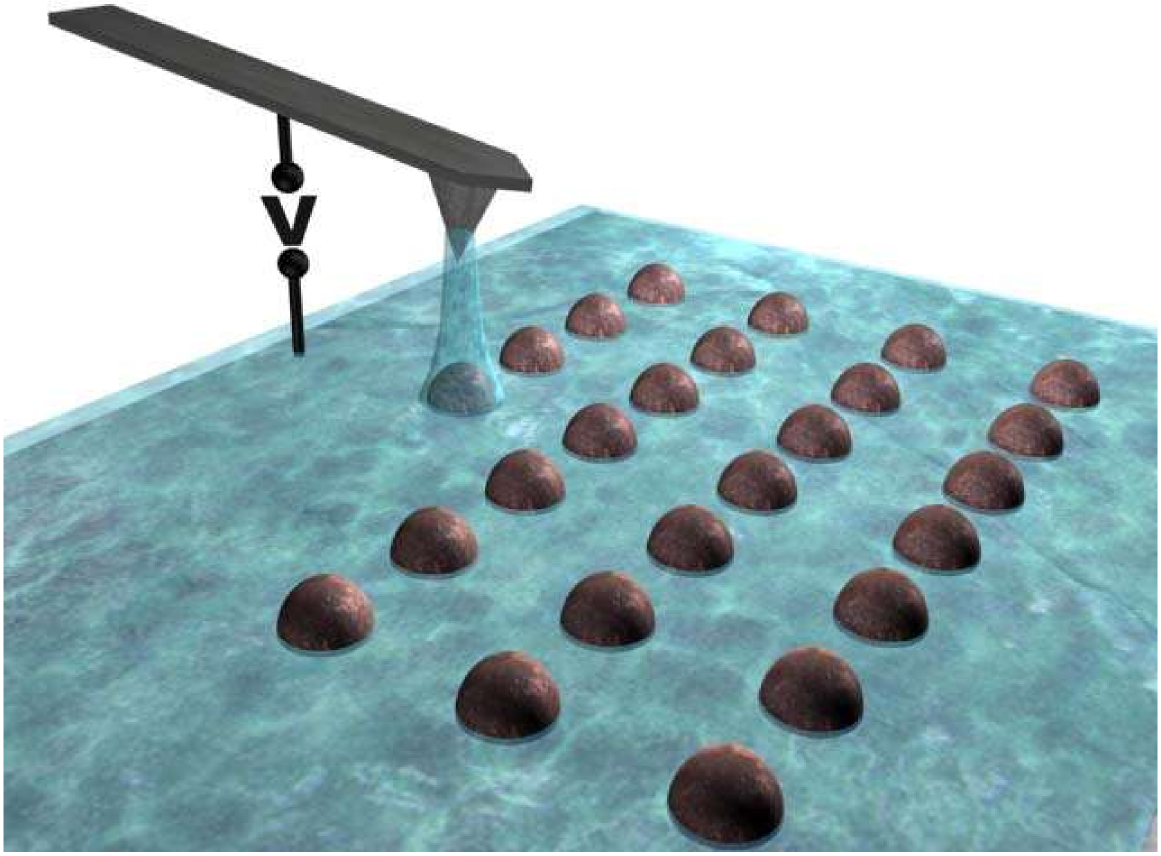
The future of nanoimprint

Nanoimprint lithography is a simple pattern transfer process that is neither limited by diffraction nor scattering effects nor secondary electrons, and does not require any sophisticated radiation chemistry. It is also a potentially simple and inexpensive technique. However, a lingering barrier to nanometer-scale patterning is the current reliance on other lithography techniques to generate the template. It is possible that self-assembled structures will provide the ultimate solution for templates of periodic patterns at scales of 10 nm and less. It is also possible to resolve the template generation issue by using a programmable template in a scheme based on double patterning.

As of October 2007, Toshiba is the only company to have validated nanoimprint lithography for 22 nm and beyond. What is more significant is that nanoimprint lithography is the first sub-30 nm lithography to be validated by an industrial user.

Chapter- 6

Local Oxidation Nanolithography



Local oxidation procedure: 3D representation the Local Oxidation Nanolithography process. A voltage pulse applied between the AFM tip and the scanned surface yields to the formation of a liquid meniscus that confines a nanometric oxidation reaction.

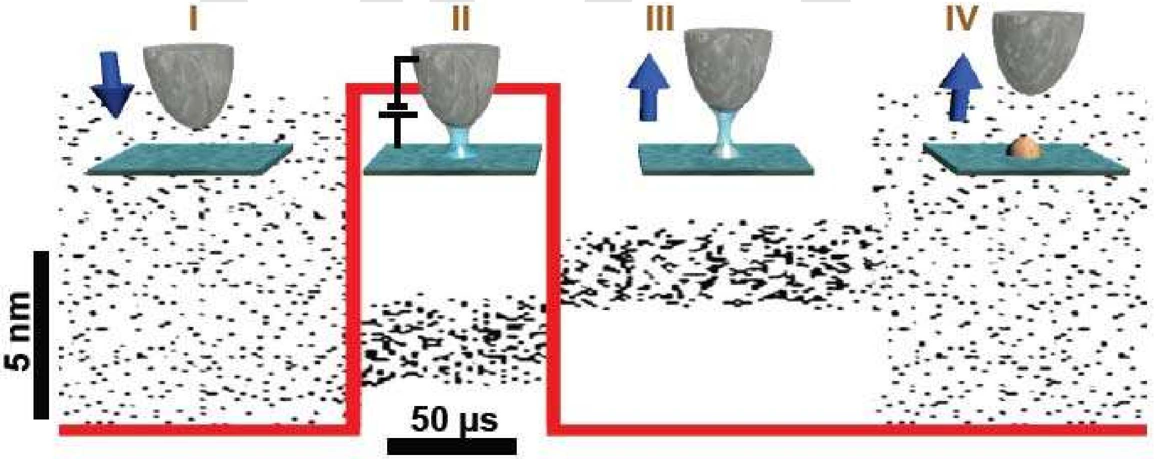
Local oxidation nanolithography (LON) is a tip-based nanofabrication method. It is based on the spatial confinement on an oxidation reaction under the sharp tip of an atomic force microscope.

The first materials on which LON was demonstrated were Si(111) and polycrystalline tantalum. Subsequently, the technique has been extended to III–V semiconductors, silicon carbide, metals such as titanium, tantalum, aluminium, molybdenum, nickel and niobium; thin films of manganite in the perovskite form; dielectrics like silicon nitride, organosilane self-assembled monolayers, dendritic macromolecules and carbonaceous films.

History

The local oxidation of a surface by means of a scanning probe technique was first observed by Dagata and co-workers in 1990 who locally modified a hydrogen-terminated silicon surface into silicon dioxide by applying a bias voltage between the tip of a scanning tunneling microscope and the surface itself. In 1993 Day and Allee demonstrated the possibility of performing local oxidation experiments with an atomic force microscope, which opened the way to applying the technique to a large variety of materials.

Basic principle



Steps of the local oxidation process in noncontact mode. I: The tip is scanning the sample in noncontact mode oscillating at a constant amplitude. II:When the voltage pulse is applied a liquid meniscus between tip and sample is induced by the electrical field. This liquid meniscus acts like a nanometer-size electrochemical cell where an oxidation reaction is held. III:When the voltage pulse is off, the AFM feedbacks withdraw the tip from the sample stretching the liquid meniscus. IV: After the meniscus is broken the tip recovers its original oscillation amplitude and continues the scanning.

Currently, local oxidation experiments are performed with an atomic force microscope operated in contact or noncontact mode with additional circuits to apply voltage pulses between tip and sample. The local oxidation process is mediated by the formation of a water meniscus.

In order to perform Local Oxidation Nanolithography, the relative humidity in the AFM chamber is kept between 30% and 60%. A voltage pulse is applied between a conductive AFM tip and the sample. The applied voltage induces the formation of a water bridge between tip and sample whenever the amplitude of the voltage pulse is above a certain threshold voltage. When the liquid meniscus is created the applied voltage pulse causes an oxidation reaction by breaking the covalent bonds in the water molecules. The liquid bridge provides the oxyanions (OH^-,O^-) needed to form the oxide and confines the lateral extension of the region to be oxidized.

The chemical reactions that govern the Local Oxidation in a metallic substrate (M) are the following:

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

$$M^n + 2nH_2O + 2ne^- \rightarrow nH_2 + 2nOH^- + M$$

while hydrogen gas is liberated at the AFM tip through the reduction reaction:

$$2H^+ + 2e^- \rightarrow H_2$$

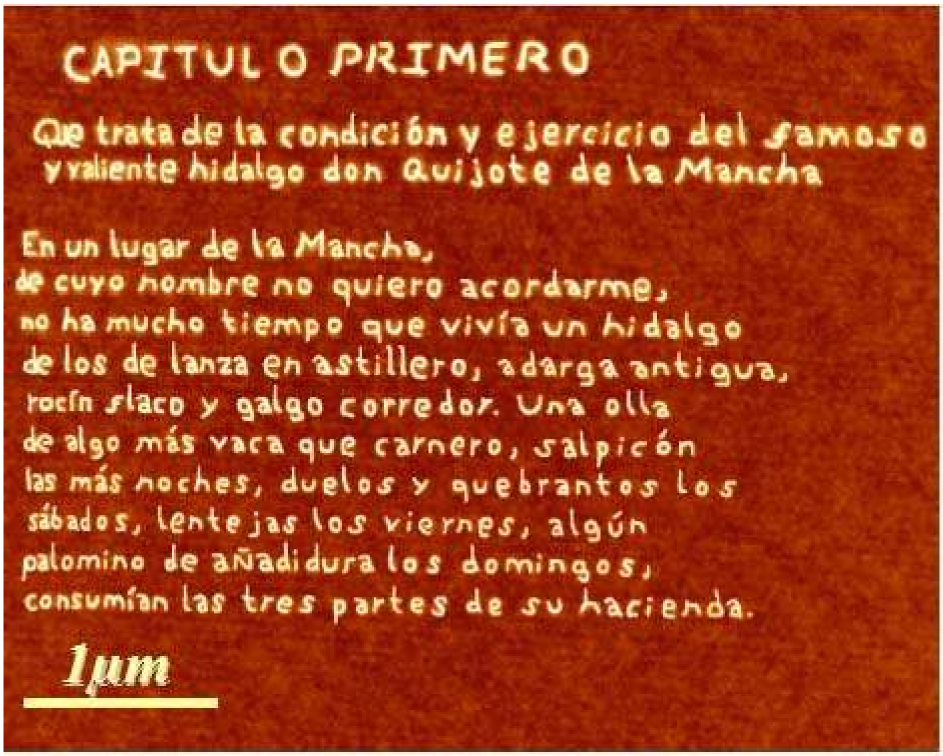
When the voltage pulse is off the AFM feedback forces the cantilever to recover its original oscillation amplitude withdrawing the tip from the sample and breaking the liquid meniscus. Finally the AFM continues to scan the sample thus allowing to image MO_n nanostructure fabricated during the Local Oxidation process with the very same tip used for its fabrication.

The method to form liquid bridges is so precise that water meniscus diameters of 20 nm or below are easily obtained. This has led to the reproducible fabrication of sub-10 nm structures in silicon and other metallic surfaces.

Experimental setup

Local oxidation experiments can be performed with almost any kind of atomic force microscope. The key requirement is the possibility to apply voltage pulses between the tip and the sample. It is recommendable to enclose the microscope in a chamber where the atmosphere is controlled. In the simplest case, the oxidant is water vapor, which is naturally present in the air. Controlling the relative humidity generally helps to obtain more reproducible results. The size of the fabricated features depends on a number of parameters, such as the distance between the sample and the tip, the amplitude and the duration of the voltage pulse, and the relative humidity of the atmosphere.

Applications



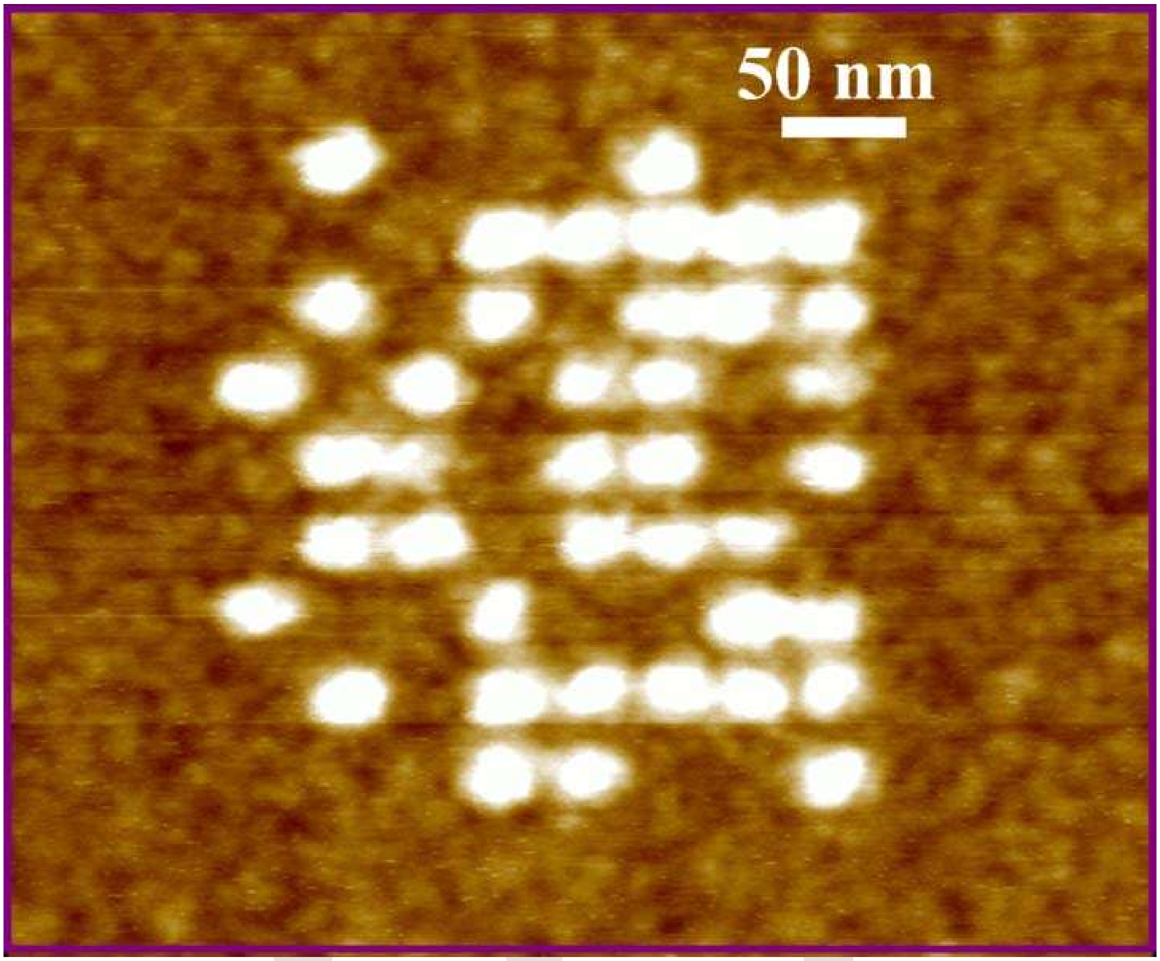
First paragraph of Cervantes' *Don Quixote* written on a silicon chip. The local oxidation technique would allow to write all the book (more than 1,000 pages) on a surface as big as the tip of one human hair.

The development of nanometer-scale lithographies is the focus of an intense research activity because progress on nanotechnology depends on the capability to fabricate, position and interconnect nanometer-scale structures.

Patterning

Local Oxidation Nanolithography allows to create a large variety of motives like dots, lines and letters with nanometer accuracy. In 2005, researchers at the Spanish National Research Council in Madrid wrote the first ten lines of Cervantes' *Don Quixote* on a few square microns of silicon. This pattern versatility can be used for information storage or to design etch-resistant nanomasks in order to fabricate nanodevices as well as many other applications.

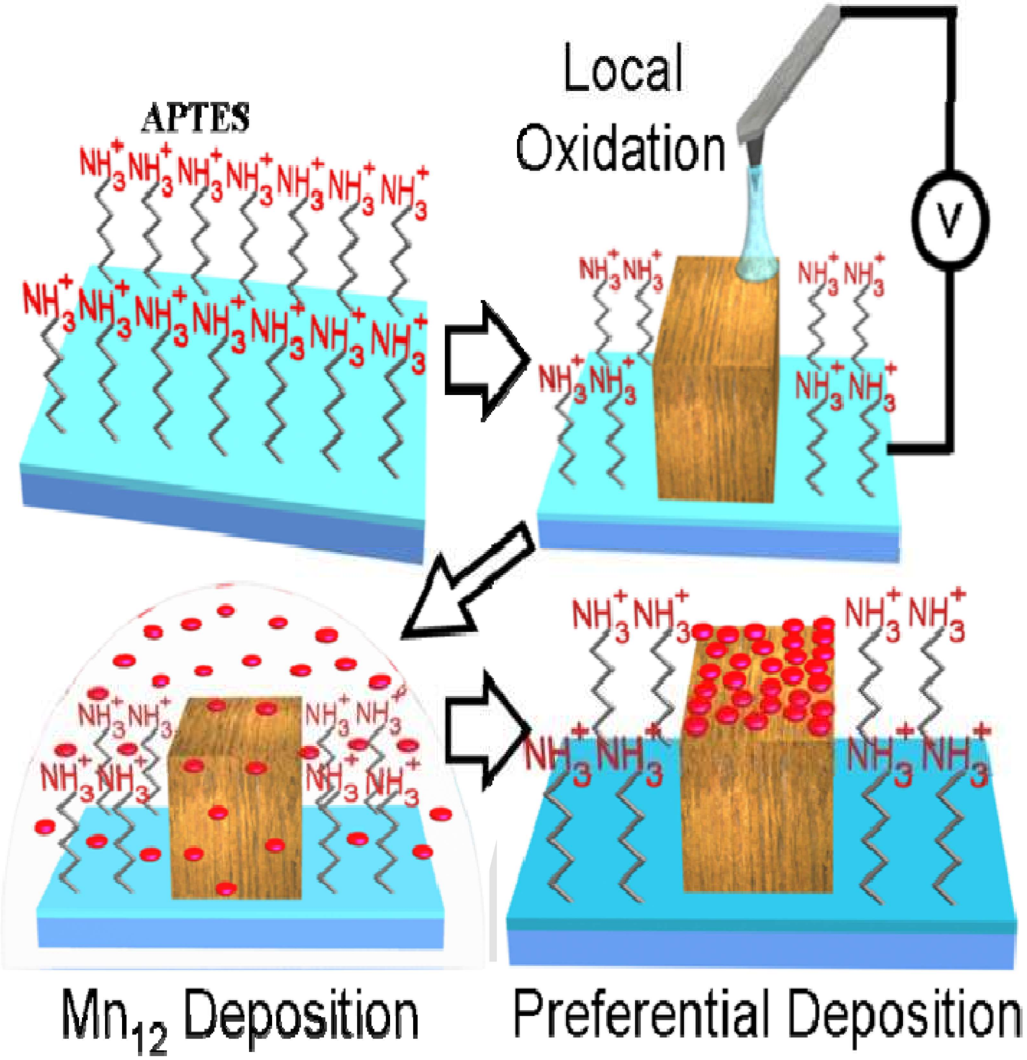
Data storage



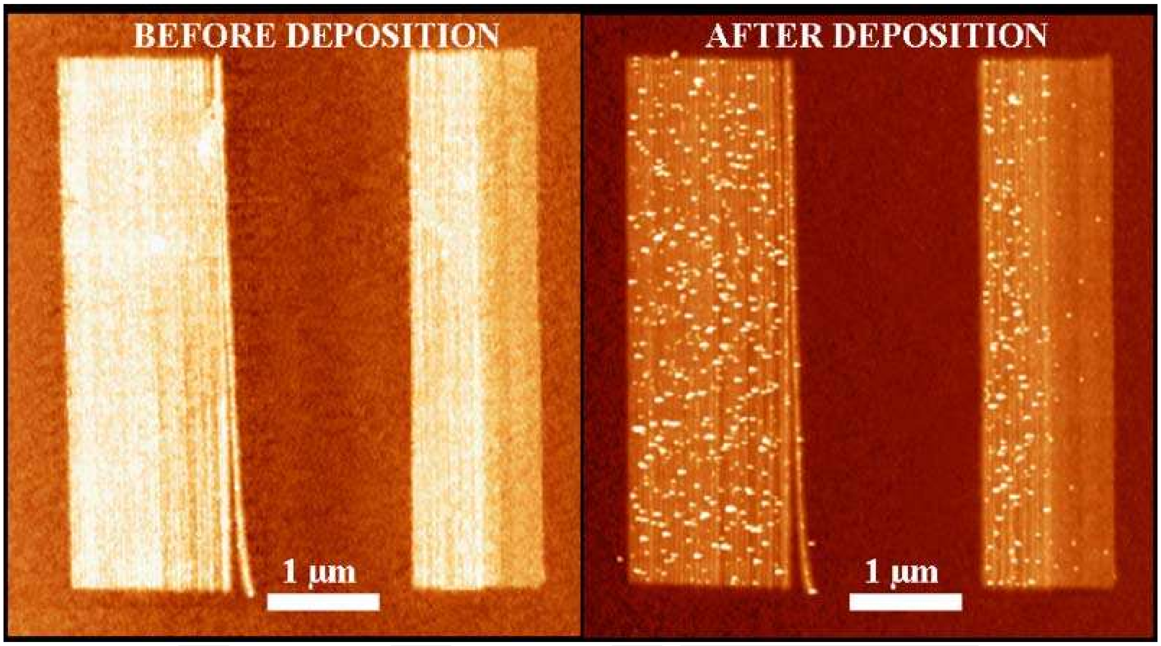
π number with twenty decimals: 3,1415926535 8979323846 written in binary code by Local Oxidation on a silicon surface.

It is possible to store information using dot-like nanostructures created by the local oxidation of a surface. This storage uses the binary code considering the presence of a nanostructure as a 1 and its lack as a 0. In this way information can be stored in a small surface with a single SiO_2 dot constituting a bit. In 1999 Cooper *et al.* demonstrated that this methods allows to obtain an information density of 1.6 Tbit/in^2. However, only read-only memories can be fabricated with this technique.

Molecular template growth and preferencial deposition



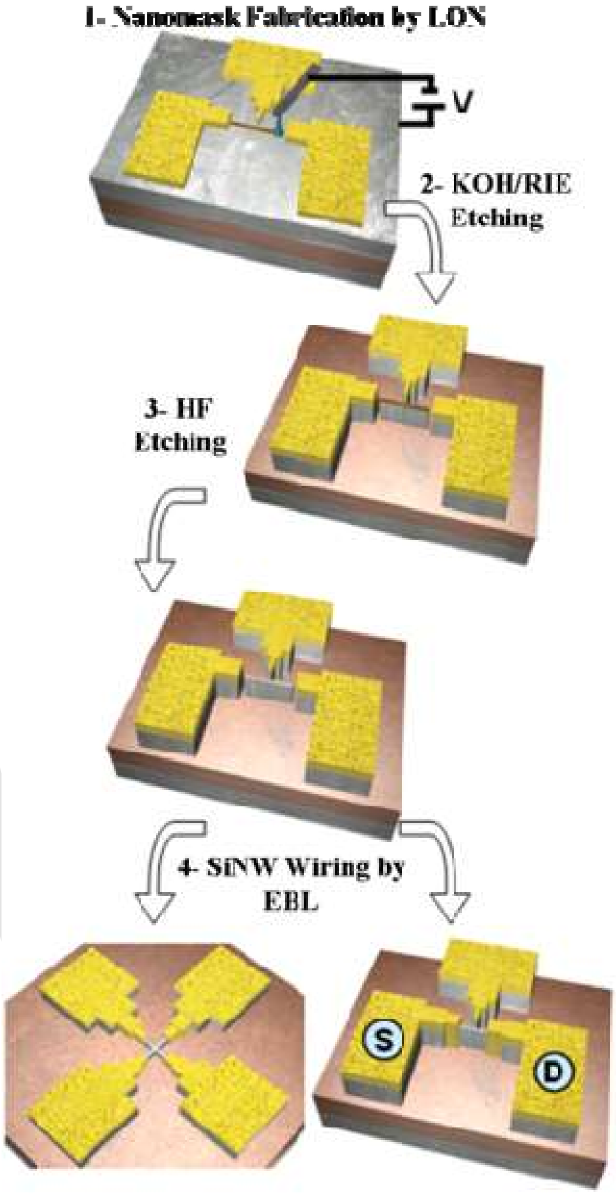
Using specific functionalizations it is possible to deposit molecules and nanoparticles only in very small domains over a substrate surface. LON is a powerful technique to fabricate this kind of domains for the preferential growth.



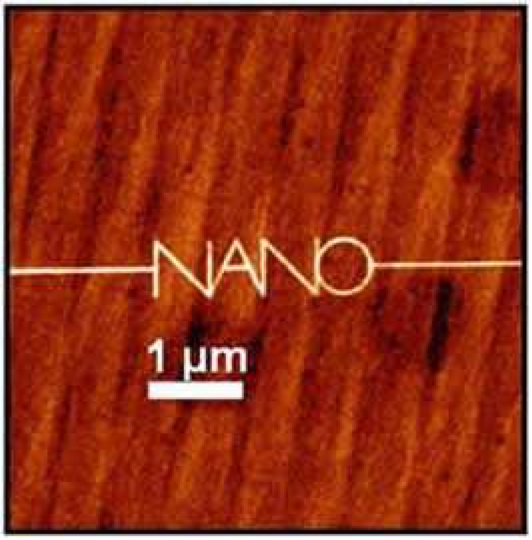
Two SiO_2 stripes were fabricated by LON over a substrate functionalized with APTES. After the deposition of a 0.1mM solution of Mn_{12} the single molecule magnets are deposited only over the regions defined by the AFM.

Local oxidation of silicon surfaces by noncontact atomic-force microscopy is an emerging and promising method for patterning surfaces at the nanometer scale due to its very precise control of the feature size. The features created with this technique can be used for the template growth and preferencial deposition of different molecules like single molecule magnets, biomolecules and conjugated organic molecules. This method of nanopositioning is an important tool for the fabrication of new nanodevices based on the novel properties exhibited by some nanoparticles and molecules. Potential applications of single-molecule magnets (SMMs) such as Mn12 as bits for information storage or qubits for quantum computation require methods for nanoscale-controlled positioning and/or manipulation of those molecules. The patterning of the Mn_{12} molecules on a silicon surface is achieved by first derivatizing this surface with a self-assembled monolayer of APTES, which leaves it terminated by amino groups ($-NH_2$). Such termination electrostatically repels the Mn12 molecules. Subsequently, a pattern of silicon dioxide is defined by LON. The SMM molecules are predominantly deposited on the oxide motives because of electrostatic attraction. The electrostatic attraction between the silicon oxide fabricated by LON and the Mn_{12} molecules achieves the preferential deposition of this molecules with a nanoscale accuracy.

Fabrication of nanodevices



In order to fabricate SiNW using the Top-Down approach of the nanotechnology a nanomask is fabricated by LON over a Silicon On Insulator substrate. After the SOI etching a SiNW is defined under the nanomask. Then the nanomask is removed with a HF etching and finally the SiNW is connected to the whole circuit using Electron Beam lithography.



SiNW nanotransistor fabricated with the term 'NANO'. This pattern exhibits a good electrical response based on in the SiNW properties only.

By using local oxidation nanolithography as tool for the fabrication of etch-resistant nanomasks, it is possible to fabricate nanoscale electronic devices, such as field effect transistors, single electron transistors, Josephson junctions, quantum rings or SQUIDs. LON also allows to fabricate silicon nanowires (SiNWs) in a top-down fashion starting from silicon on insulator (SOI) wafers. Local oxidation nanolithography contributes to the nanometric precision of the device fabrication. This top-down fabrication technique allows the fabrication of a large variety of SiNWs with different shapes, from angular to circular. It also allows the precise positioning of the silicon nanowires in ant desired position, making easier its integration; indeed, this technique is compatible with the standard silicon CMOS processing technology. Single crystalline silicon nanowires have already shown a great potential as ultrasensitive sensors by detecting changes in the nanowire conductivity when a specific analyte is present. Local oxidation nanolithography, therefore, is a promising technique to allow the realisation of array of biosensors.

Chapter- 7

Dip-Pen Nanolithography

Introduction

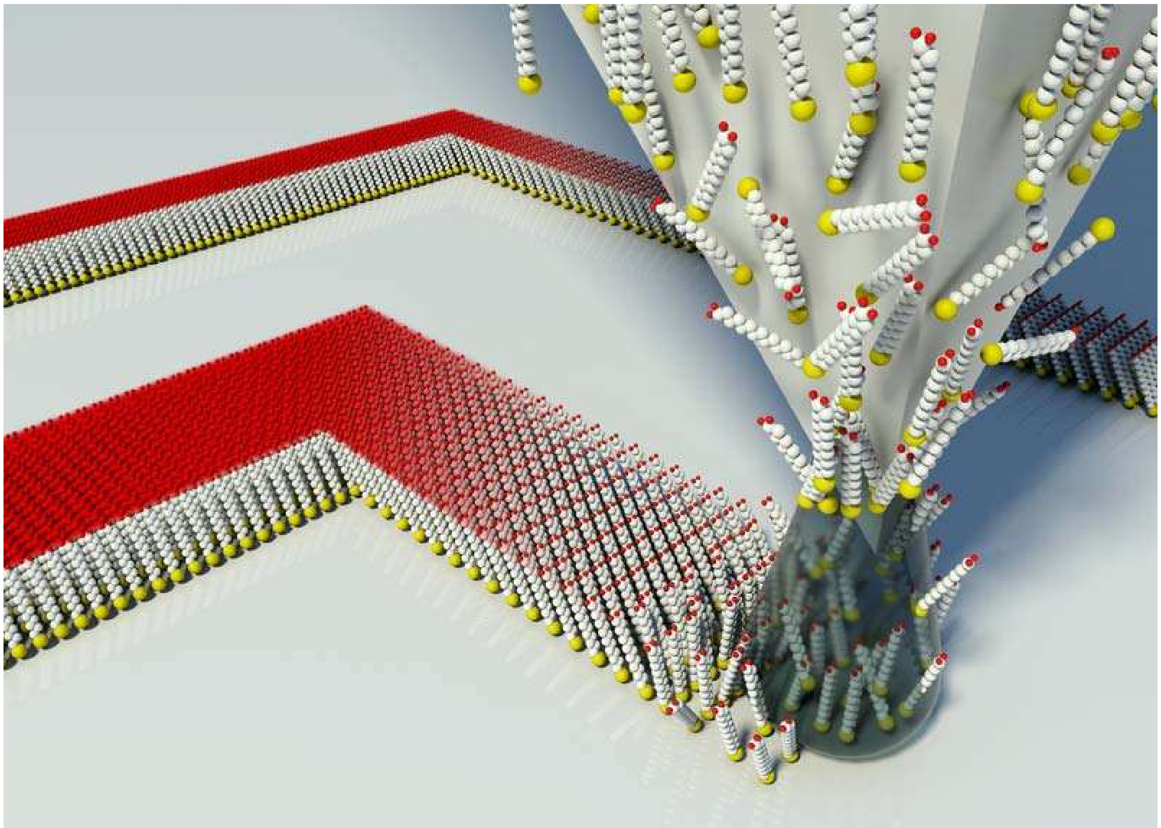
Dip Pen Nanolithography (DPN) began as a scanning probe lithography technique where an atomic force microscope tip was used to transfer alkane thiolates to a gold surface. This technique allows surface patterning on scales of under 100 nanometers. DPN is the nanotechnology analog of the dip pen (also 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. Recent advances have demonstrated massively parallel patterning using two-dimensional arrays of 55,000 tips. Applications of this technology currently range through chemistry, materials science, and the life sciences, and include such work as ultra high density biological nanoarrays, and additive photomask repair.

The uncontrollable transfer of a molecular 'ink' from a coated AFM tip to a substrate was first reported by Jaschke and Butt in 1995, but they erroneously concluded that alkanethiols could not be transferred to gold substrates to form stable nanostructures. A research group at Northwestern University led by Chad Mirkin studied the process and determined that under the appropriate conditions, molecules could be transferred to a wide variety of surfaces to create stable chemically-adsorbed monolayers in a high resolution lithographic process they termed "DPN" . Mirkin and his coworkers hold the patents on this process, and the patterning technique has expanded to include liquid "inks". It is important to note that "liquid inks" are governed by a very different deposition mechanism when compared to "molecular inks".

Deposition Materials

Molecular Inks



Classic DPN mechanism: Molecular ink diffusing from a nanoscale tip to a surface through a water meniscus.

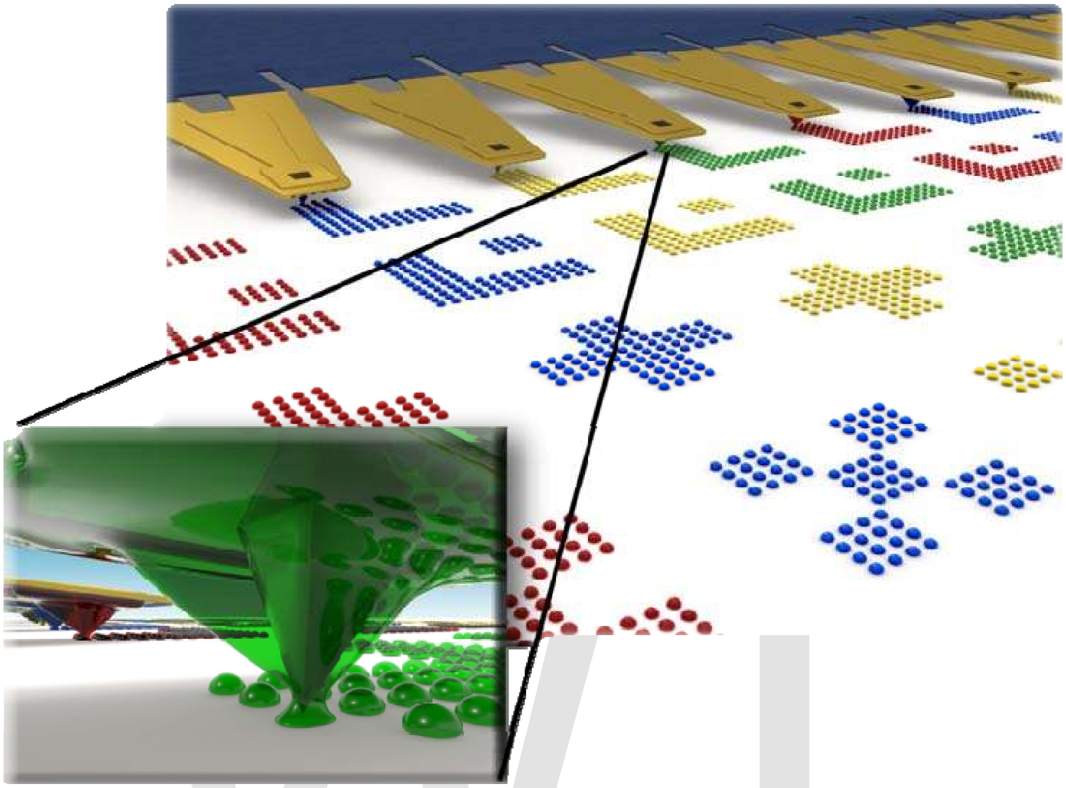
Molecular inks are typically composed of small molecules that are coated onto a DPN tip and are delivered to the surface through a water meniscus. In order to coat the tips, one can either vapor coat the tip or dip the tips into a dilute solution containing the molecular ink. If one dip-coats the tips, the solvent must be removed prior to deposition. The deposition rate of a molecular weight is dependent on the diffusion rate of the molecule, which is different for each molecule. The size of the feature is controlled by the tip/surface dwell-time (ranging from milliseconds to seconds) and the size of the water meniscus, which is determined by the humidity conditions (assuming the tip's radius of curvature is much smaller than the meniscus).

- Water meniscus mediated (exceptions do exist)
- Nanoscale feature resolution (50 nm to 2000 nm)
- No multiplexed depositions
- Each molecular ink is limited to its corresponding substrate

Examples

- Alkane thiols written to gold
- Silanes written to glass or silicon

Liquid Inks



Liquid ink deposition mechanism

Liquid inks can be any material that is liquid at deposition conditions. The liquid deposition properties are determined by the interactions between the liquid and the tip, the liquid and the surface, and the viscosity of the liquid itself. These interactions limit the minimum feature size of the liquid ink to about 1 micron, depending on the contact angle of the liquid. Higher viscosities offer greater control over feature size and are desirable. Unlike molecular inks, it is possible to perform multiplexed depositions using a carrier liquid. For example, using a viscous buffer, it is possible to directly deposit multiple proteins simultaneously.

- 1-10 micron feature resolution
- Multiplexed depositions
- Less restrictive ink/surface requirements
- Direct deposition of high viscosity materials

Examples

Gel

An upturned vial of hair gel

A **gel** (from the lat. *gelu*—freezing, cold, ice or *gelatus*—frozen, immobile) is a solid, jelly-like material that can have properties ranging from soft and weak to hard and tough. Gels are defined as a substantially dilute cross-linked system, which exhibits no flow when in the steady-state. By weight, gels are mostly liquid, yet they behave like solids due to a three-dimensional cross-linked network within the liquid. It is the crosslinks within the fluid that give a gel its structure (hardness) and contribute to stickiness (tack). In this way gels are a dispersion of molecules or particles within a liquid in which the solid is the continuous phase and the liquid is the discontinuous phase.

Composition

Gels consist of a solid three-dimensional network that spans the volume of a liquid medium and ensnares it through surface tension effects. This internal network structure may result from physical bonds (**physical gels**) or chemical bonds (**chemical gels**), as well as crystallites or other junctions that remain intact within the extending fluid. Virtually any fluid can be used as an extender including water (hydrogels), oil, and air (aerogel). Both by weight and volume, gels are mostly fluid in composition and thus exhibit densities similar to those of their constituent liquids. Edible jelly is a common example of a hydrogel and has approximately the density of water.

Cationic polymers

Cationic polymers are positively charged polymers. Their positive charges prevent the formation of coiled polymers. This allows them to contribute more to viscosity in their stretched state, because the stretched-out polymer takes up more space than a coiled polymer and this resists the flow of solvent molecules around it. Cationic polymers are a main functional component of hair gel, because the positive charged polymers also bind the negatively charged amino acids on the surface of the keratin molecules in the hair. More complicated polymer formulas exist, e.g., a copolymer of vinylpyrrolidone, methacrylamide, and hydrogel N-vinylimidazole. In certain concentrations, dispersions of lyophilic colloids tend to form solid masses, particularly when the solubility of the colloidal material is reduced by change in temperature. These semi-solids are known as gels. The settings of solutions of gelatin and agar on cooling are well known examples of gel formation

Types of gels

Hydrogels

Hydrogel (also called aquagel) is a network of polymer chains that are hydrophilic, sometimes found as a colloidal gel in which water is the dispersion medium. Hydrogels are highly absorbent (they can contain over 99% water) natural or synthetic polymers. Hydrogels also possess a degree of flexibility very similar to natural tissue, due to their significant water content. Common uses for hydrogels include

- currently used as scaffolds in tissue engineering. When used as scaffolds, hydrogels may contain human cells to repair tissue.
- environmentally sensitive hydrogels which are also known as 'Smart Gels' or 'Intelligent Gels'. These hydrogels have the ability to sense changes of pH, temperature, or the concentration of metabolite and release their load as result of such a change.
- as sustained-release drug delivery systems.
- provide absorption, desloughing and debriding capacities of necrotics and fibrotic tissue.
- hydrogels that are responsive to specific molecules, such as glucose or antigens can be used as biosensors, as well as in DDS.
- used in disposable diapers where they "capture" urine, or in sanitary napkins
- contact lenses (silicone hydrogels, polyacrylamides)
- medical electrodes using hydrogels composed of cross-linked polymers (polyethylene oxide, polyAMPS and polyvinylpyrrolidone)
- water gel explosives
- rectal drug delivery and diagnosis

Other, less common uses include

- breast implants

- granules for holding soil moisture in arid areas
- dressings for healing of burn or other hard-to-heal wounds. Wound gels are excellent for helping to create or maintain a moist environment.
- reservoirs in topical drug delivery; particularly ionic drugs, delivered by iontophoresis

Common ingredients are e.g. polyvinyl alcohol, sodium polyacrylate, acrylate polymers and copolymers with an abundance of hydrophilic groups.

Natural hydrogel materials are being investigated for tissue engineering; these materials include agarose, methylcellulose, hyaluronan, and other naturally derived polymers.

Organogels

An **organogel** is a non-crystalline, non-glassy thermoreversible (thermoplastic) solid material composed of a liquid organic phase entrapped in a three-dimensionally cross-linked network. The liquid can be, for example, an organic solvent, mineral oil, or vegetable oil. The solubility and particle dimensions of the structurant are important characteristics for the elastic properties and firmness of the organogel. Often, these systems are based on self-assembly of the structurant molecules.

Organogels have potential for use in a number of applications, such as in pharmaceuticals, cosmetics, art conservation, and food. An example of formation of an undesired thermoreversible network is the occurrence of wax crystallization in petroleum.

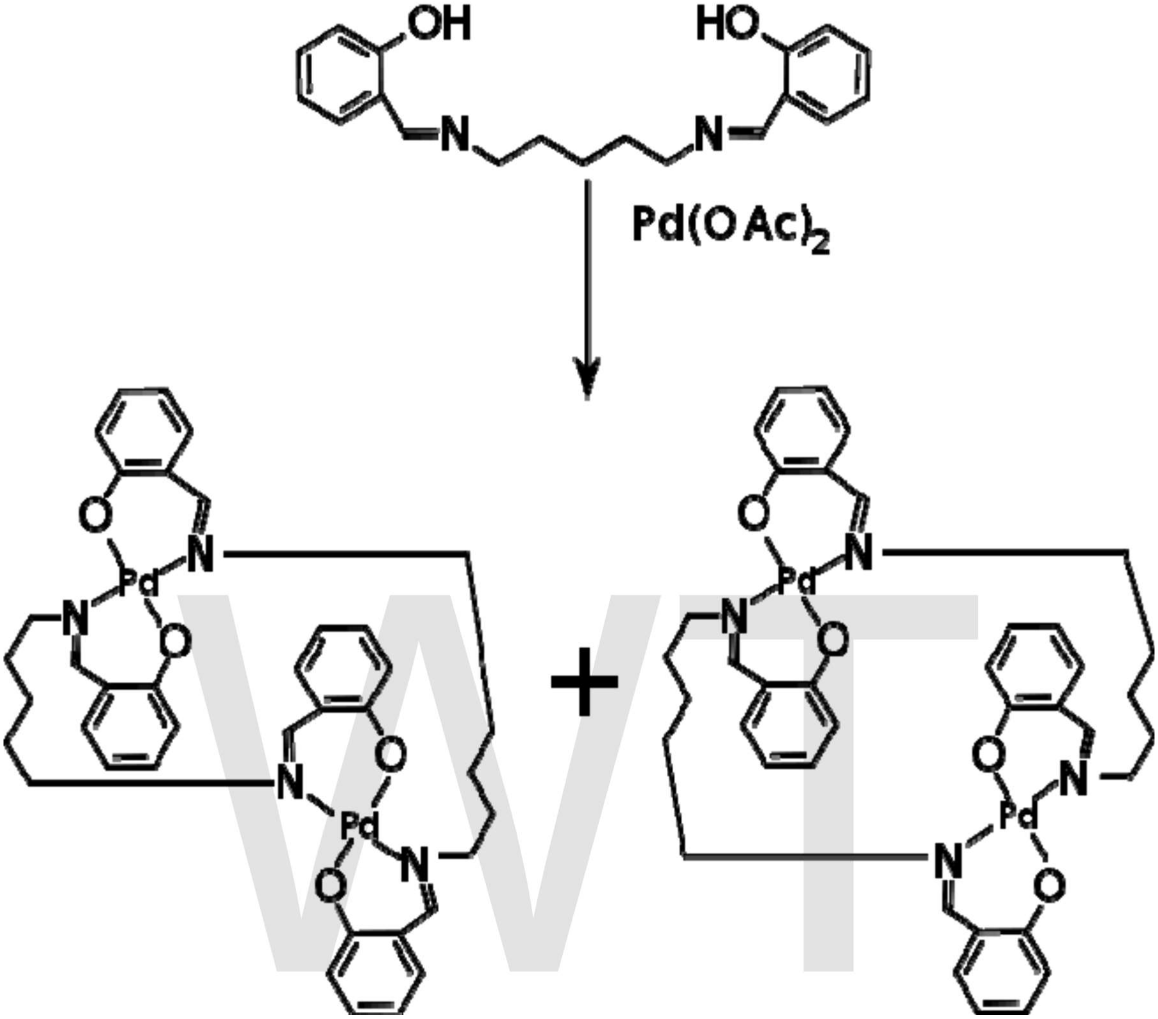
Xerogels

A **xerogel** is a solid formed from a gel by drying with unhindered shrinkage. Xerogels usually retain high porosity (25%) and enormous surface area (150–900 m^2/g), along with very small pore size (1-10 nm). When solvent removal occurs under hypercritical (supercritical) conditions, the network does not shrink and a highly porous, low-density material known as an *aerogel* is produced. Heat treatment of a xerogel at elevated temperature produces viscous sintering (shrinkage of the xerogel due to a small amount of viscous flow) and effectively transforms the porous gel into a dense glass.

Properties

Many gels display thixotropy - they become fluid when agitated, but resolidify when resting. In general, gels are apparently solid, jelly-like materials. By replacing the liquid with gas it is possible to prepare aerogels, materials with exceptional properties including very low density, high specific surface areas, and excellent thermal insulation properties.

Sound-induced gelation



The palladium complex is synthesised from palladium acetate and N,N'-Bis(salicylidene)pentamethylenediamine in boiling benzene and forms the anti conformer (left) and the syn conformer (right)

Sound-induced gelation is described in 2005 in an organopalladium compound that in solution transforms from a transparent liquid to an opaque gel upon application of a short burst (seconds) of ultrasound. Heating to above the so-called *gelation temperature* T_{gel} takes the gel back to the solution. The compound is a dinuclear palladium complex made from palladium acetate and a N,N'-bis-salicylidene diamine. Both compounds react to form an anti conformer (gelling) and a syn conformer (non-gelling) which are separated by column chromatography. In the solution phase, the dimer molecules are bent and self-locked by aromatic stacking interactions, whereas in the gel phase the conformation is planar with interlocked aggregates. The anti conformer has planar chirality and both enantiomers were separated by chiral column chromatography. The (-) anti conformer has a specific rotation of -375° but is unable to gel by itself. In the gel phase, the dimer molecules form stacks of alternating (+) and (−) components. This process starts at the onset of the sonication and proceeds even without further sonication.

Naturally occurring gels in the animal kingdom

Some species secrete gels that are effective in parasite control. For example the Long-finned pilot whale secretes an enzymatic gel that rests on the outer surface of this animal and helps prevent other organisms from establishing colonies on the surface of these dolphins' bodies.

Applications

Many substances can form gels when a suitable thickener or gelling agent is added to their formula. This approach is common in manufacture of wide range of products, from foods to paints and adhesives.

In fiber optics communications, a soft gel resembling "hair gel" in viscosity is used to fill the plastic tubes containing the fibers. The main purpose of the gel is to prevent water intrusion if the buffer tube is breached, but the gel also buffers the fibers against mechanical damage when the tube is bent around corners during installation, or flexed. Additionally, the gel acts as a processing aid when the cable is being constructed, keeping the fibers central whilst the tube material is extruded around it.

Hydrogels existing naturally in the body include mucus, the vitreous humor of the eye, cartilage, tendons and blood clots. Their viscoelastic nature results in the soft tissue component of the body, disparate from the mineral-based hard tissue of the skeletal system. Researchers are actively developing synthetically-derived tissue replacement technologies derived from hydrogels, for both temporary implants (degradable) and permanent implants (non-degradable). A review article on the subject discusses the use of hydrogels for nucleus pulposus replacement, cartilage replacement, and synthetic tissue models.

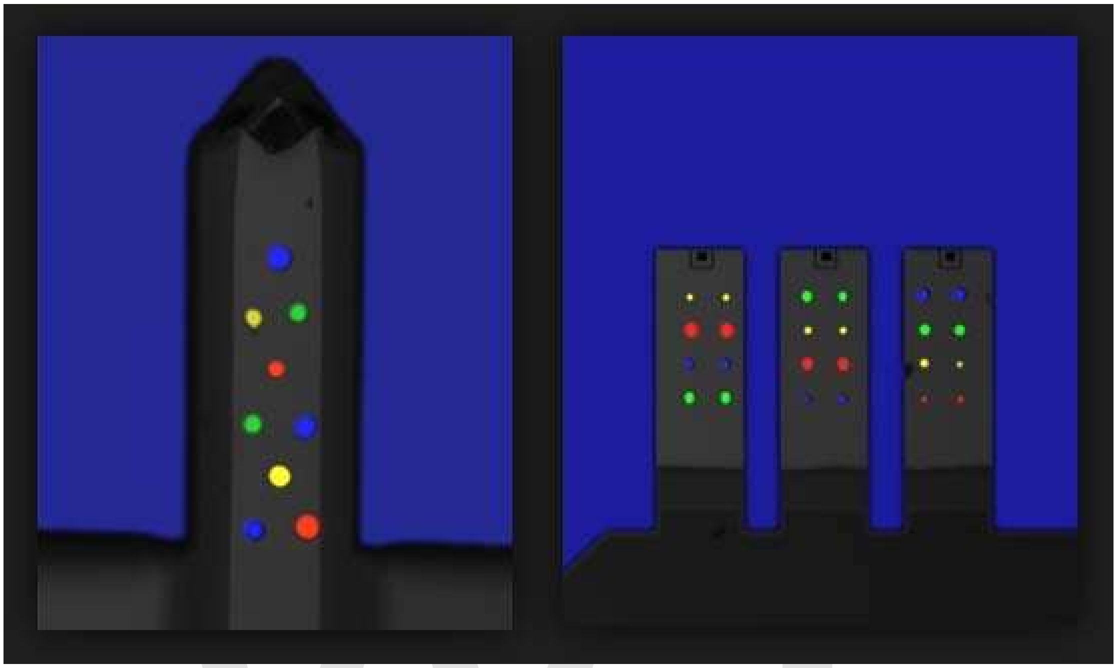
- Protein, peptide, and DNA patterning
- Sol gels
- Conductive inks
- Lipids

Applications

In order to define a good DPN application, it is important to understand what DPN can do that other techniques can't. Direct-write techniques, like contact printing, can pattern multiple biological materials but it cannot create features with subcellular resolution. Many high-resolution lithography methods can pattern at sub-micron resolution, but these require high-cost equipment that were not designed for biomolecule deposition and cell culture. Micro contact printing can print biomolecules at ambient conditions, but it cannot pattern multiple materials with nanoscale registry.

Industrial Applications

The following are some examples of how DPN is being applied to potential products.



Cantilever biosensor functionalized with 4 different proteins

1. Biosensor Functionalization - Directly place multiple capture domains on a single biosensor device
2. Nanoscale Sensor Fabrication - Small, high-value sensors that can detect multiple targets
3. Nanoscale Protein Chips - High-density protein arrays with increased sensitivity

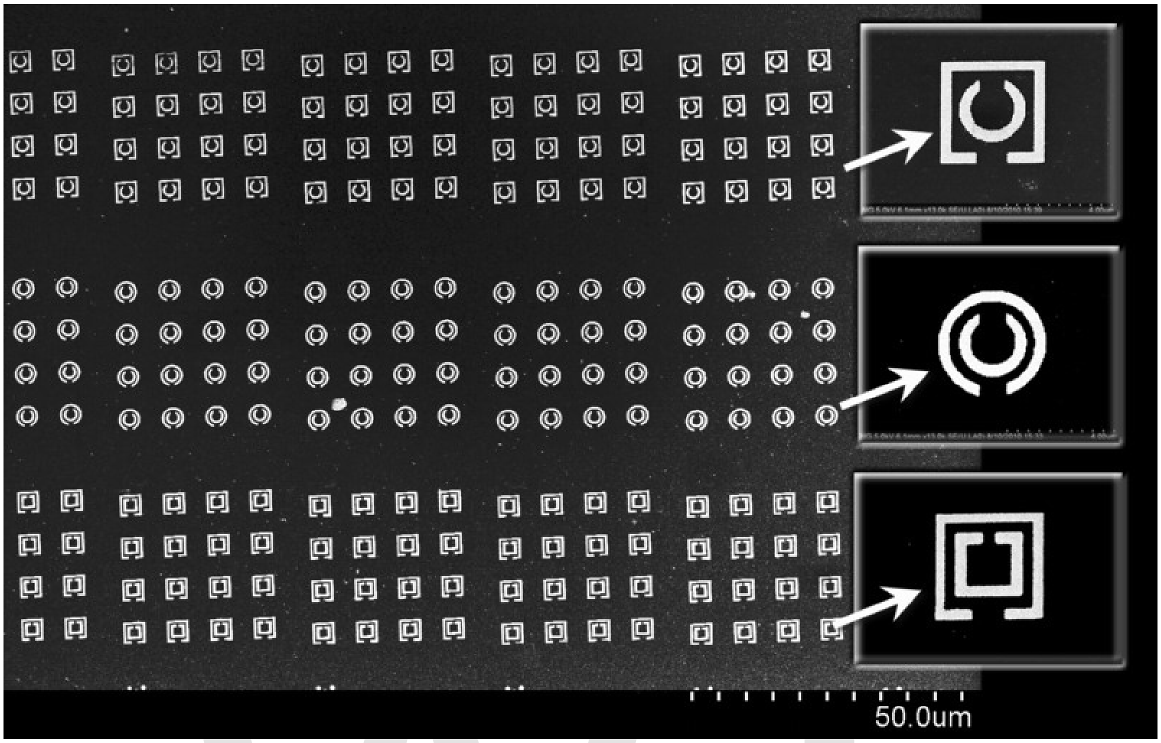
Emerging Applications

Cell Engineering

DPN is emerging as a powerful research tool for manipulating cells at subcellular resolution

- Stem cell differentiation
- Subcellular drug delivery
- Cell sorting
- Surface gradients
- Subcellular ECM protein patterns
- Cell adhesion

Rapid Prototyping



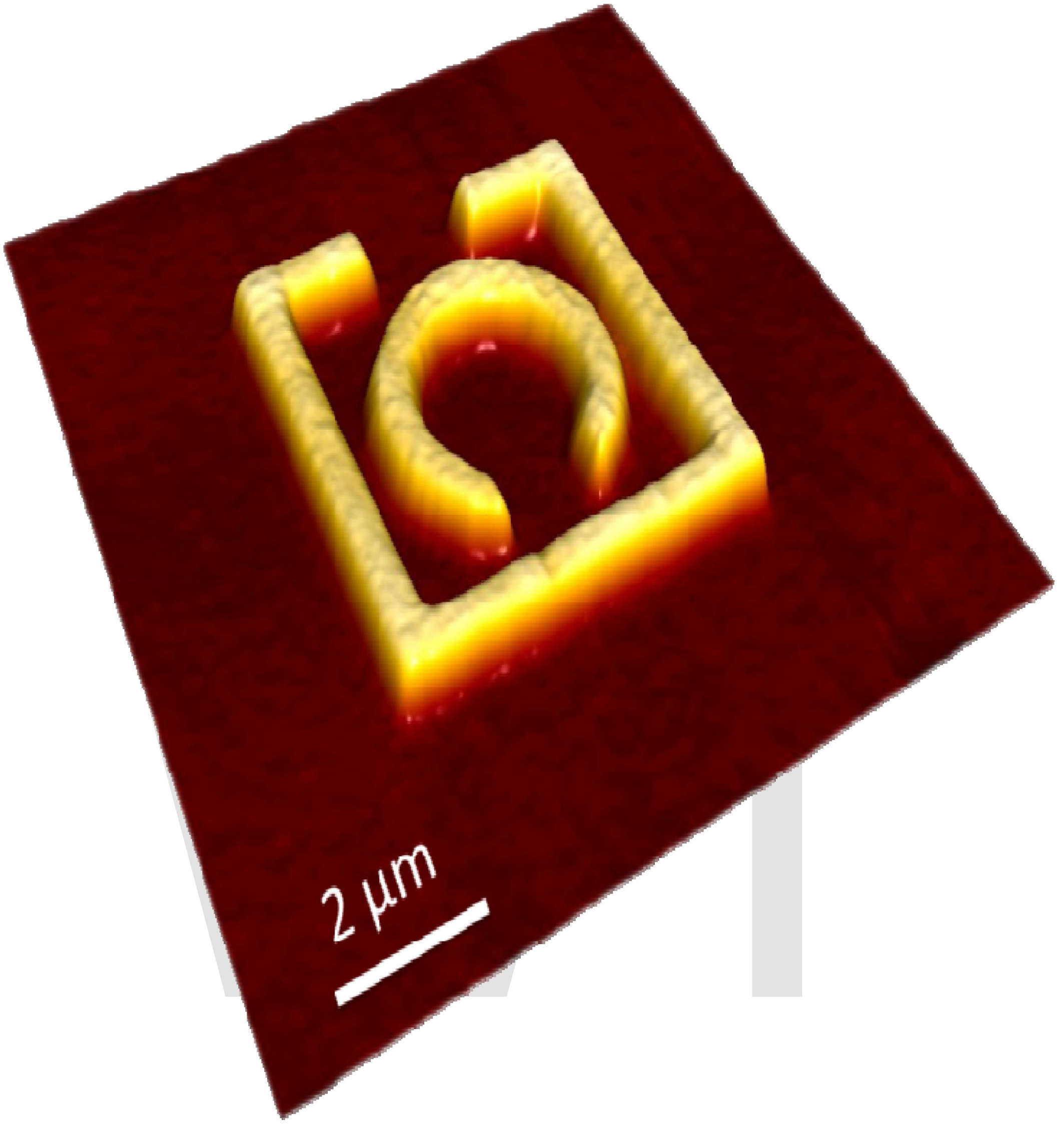
SEM image of DPN fabricated gold metastructure arrays.

- Plasmonics and Metamaterials
- Cell and tissue screening

DPN Properties

Direct Write

DPN is a direct write technique so it can be used for top-down and bottom-up lithography applications. In top-down work, the tips are used to deliver an etch resist to a surface, which is followed by a standard etching process. In bottom-up applications, the material of interest is delivered directly to the surface via the tips.



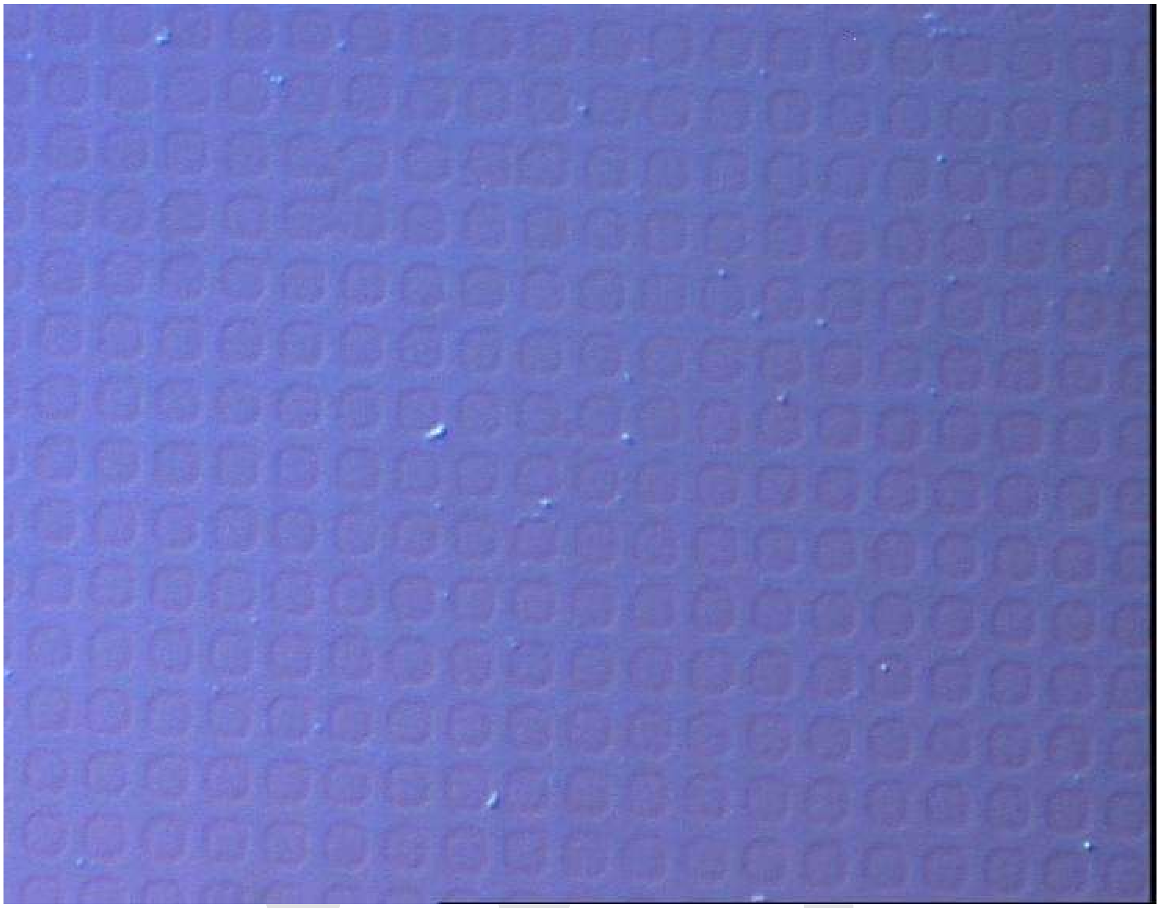
Gold on silicon metastructure fabricated with top-down DPN methods

Unique advantages

- Directed Placement - Directly print various materials onto existing nano and microstructures with nanoscale registry
- Direct Write - Maskless creation of arbitrary patterns with feature resolutions from as small as 50 nm and as large as 10 microns
- Biocompatible - Subcellular to nanoscale resolution at ambient deposition conditions
- Scalable - Force independent, allowing for parallel depositions

Common Misconceptions

Direct comparisons to other techniques



Streptavidin (4nm thickness)deposited using micro contact printing

The criticism most often directed at DPN is the patterning speed. The reason for this has more to do with how it is compared to other techniques rather than any inherent weaknesses. For example, the soft lithography method, micro contact printing (μCP), is the current standard for low cost, bench-top micro and nanoscale patterning, so it is easy to understand why DPN is compared directly to micro contact printing. The problem is that the comparisons are usually based upon applications that are strongly suited to μCP, instead of comparing them to some neutral application. μCP has the ability to pattern one material over a large area in a single stamping step, just as photolithography can pattern over a large area in a single exposure. Of course DPN is slow when it is compared to the strength of another technique. DPN is a maskless direct write technique that can be used to create multiple patterns of varying size, shape, and feature resolution, all on a single substrate. No one would try to apply micro contact printing to such a project because the it would never be worth the time and money required to fabricate each master stamp for each new pattern. Even if they did, micro contact printing would not be capable of aligning multiple materials from multiple stamps with nanoscale registry. The best way to understand this misconception is to think about the different ways to apply photolithography and e-beam lithography. No one would try to use e-beam to solve a photolithography problem and then claim e-beam to be "too slow". Directly compared to photolithography's large area patterning capabilities, e-beam lithography **is** slow and yet, e-beam instruments can be found in every lab and nanofab in the world. The reason for this is because E-beam has unique capabilities that cannot be matched by photolithography, just as DPN has unique capabilities that cannot be matched by micro contact printing.

Connection to Atomic Force Microscopy

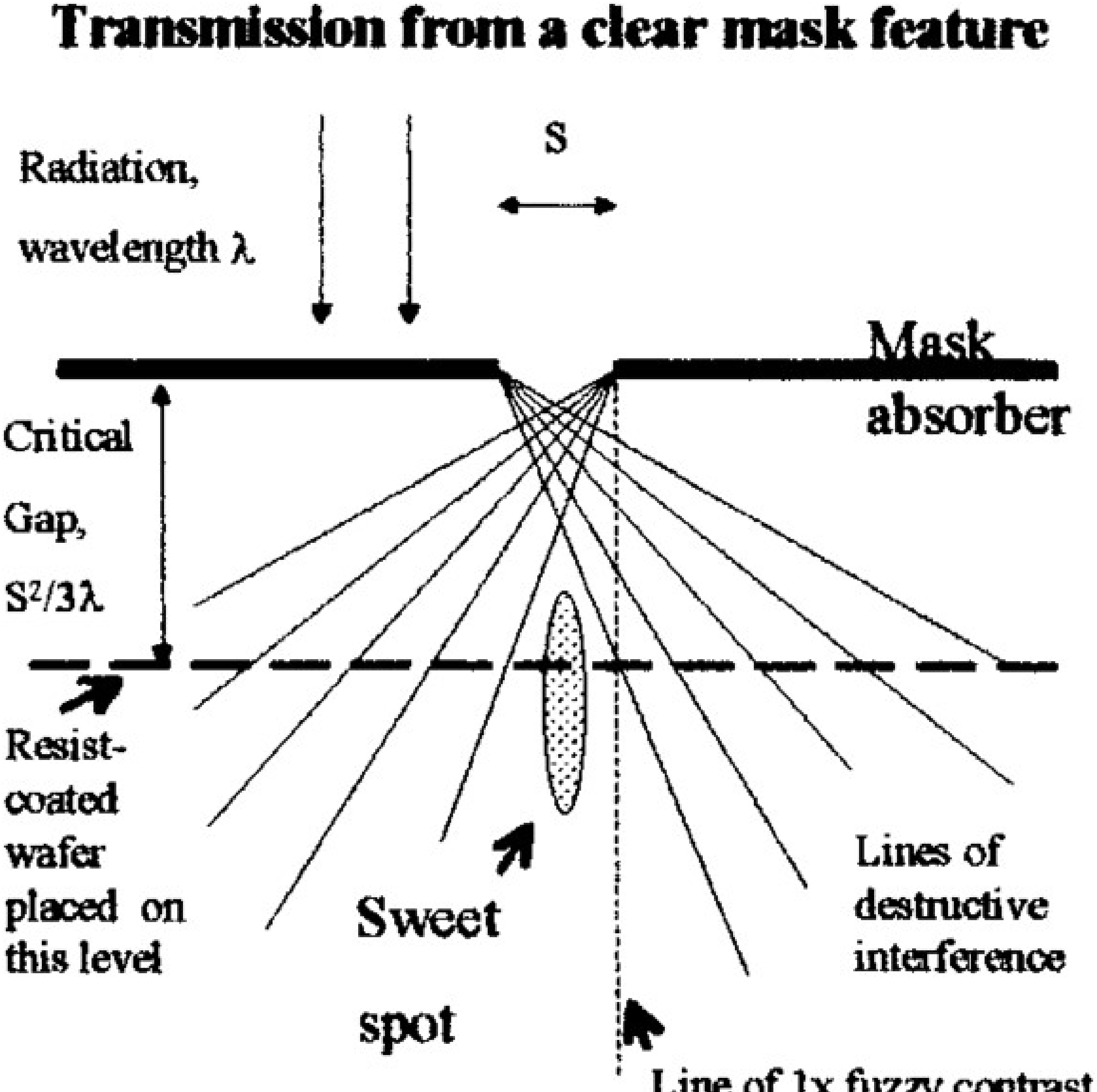
DPN evolved directly from AFM so it is not a surprise that people often assume that any commercial AFM can perform DPN experiments. In fact, DPN does not require an AFM, and an AFM does not necessarily have real DPN capabilities. There is an excellent analogy with scanning electron microscopy (SEM) and electron beam (E-beam) lithography. E-beam evolved directly from SEM technology and both use a focused electron beam, but no one would ever suggest that one could perform modern E-beam lithography experiments on a SEM that lacks the proper lithography hardware and software requirements.

It is also important to consider one of the unique characteristics of DPN, namely its force independence. With virtually all ink/substrate combinations, the same feature size will be patterned no matter how hard the tip is pressing down against the surface. As long as robust SiN tips are used, there is no need for complicated feedback electronics, no need for lasers, no need for quad photo-diodes, and no need for an AFM.

Chapter- 8

Other Techniques of Nanolithography

X-ray lithography



X-ray lithography, is a process used in electronic industry to selectively remove parts of a thin film. It uses X-rays to transfer a geometric pattern from a mask to a light-sensitive chemical photoresist, or simply "resist," on the substrate. A series of chemical treatments then engraves the produced pattern into the material underneath the photoresist.

Mechanisms

X-ray lithography originated as a candidate for next-generation lithography for the semiconductor industry, with batches of microprocessors successfully produced. Having short wavelengths (below 1 nm), X-rays overcome the diffraction limits of optical lithography, allowing smaller feature sizes. If the X-ray source isn't collimated, as with a synchrotron radiation, elementary collimating mirrors or diffractive lenses are used in the place of the refractive lenses used in optics. The X-rays illuminate a mask placed in proximity of a resist-coated wafer. The X-rays are broadband, typically from a compact synchrotron radiation source, allowing rapid exposure. Deep X-ray lithography (DXRL) uses yet shorter wavelengths on the order of 0.1 nm and modified procedures such as the LIGA process, to fabricate deep and even three-dimensional structures.

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 (without magnification) on the line of fuzzy contrast as illustrated in the figure. However, with the increasing need for high resolution, X-ray lithography is now performed on what is called the "sweet spot", using local "demagnification by bias". Dense structures are developed by multiple exposures with translation. The advantages of using 3x demagnification include, 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.

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, which is determined by wavelength and gap, the image exposure contrast *(max-min)/(max+min)* is reduced because the pitch is on the order of the primary photo-electron range. The sidewall roughness and slopes are influenced by these secondary electrons as they can travel few micrometers in the area under the absorber, depending on exposure X-ray energy. 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.

Photoelectrons, secondary electrons and Auger electrons

Secondary electrons have energies of 25 eV or less, and can be generated by any ionizing radiation (VUV, EUV, X-rays, ions and other electrons). Auger electrons have energies of hundreds of electronvolts. The secondaries (generated by and outnumbering the Auger and primary photoelectrons) are the main agents for resist exposure.

The relative ranges of photoelectron primaries and Auger electrons depend on their respective energies. These energies depend on the energy of incident radiation and on the composition of the resist. There is considerable room for optimum selection. When Auger electrons have lower energies than primary photoelectrons, they have shorter ranges. Both decay to secondaries which interact with chemical bonds. When secondary energies are too low, they fail to break the chemical bonds and cease to affect print resolution. Experiments prove that the combined range is less than 20 nm. On the other hand, the secondaries follow a different trend below ≈30 eV: the lower the energy, the longer the mean free path though they are not then able to affect resist development.

As they decay, primary photo-electrons and Auger electrons eventually become physically indistinguishable (as in Fermi–Dirac statistics) from secondary electrons. The range of low-energy secondary electrons is sometimes larger than the range of primary photo-electrons or of Auger electrons. What matters for X-ray lithography is the effective range of electrons that have sufficient energy to make or break chemical bonds in negative or positive resists.

Lithographic electron range

X-rays do not charge. The relatively large mean free path (~20 nm) of secondary electrons hinders resolution control at nanometer scale. In particular, electron beam lithography suffers negative charging by incident electrons and consequent beam spread which limits resolution. It is difficult therefore to isolate the effective range of secondaries which may be less than 1 nm.

The combined electron mean free path results in an image blur, which is usually modeled as a Gaussian function (where σ = blur) that is convolved with the expected image. As the desired resolution approaches the blur, the *dose image* becomes broader than the *aerial image* of the incident X-rays. The blur that matters is the *latent image* that describes the making or breaking of bonds during the exposure of resist. The *developed image* is the final relief image produced by the selected high contrast development process on the latent image.

The range of primary, Auger, secondary and ultralow energy higher-order generation electrons which print (as STM studies proved) can be large (tens of nm) or small (nm), according to various cited publications. Because this range is not a fixed number, it is hard to quantify. Line edge roughness is aggravated by the associated uncertainty. Line edge roughness is supposedly statistical in origin and only indirectly dependent on mean range. Under commonly practiced lithography conditions, the various electron ranges can be controlled and utilized.

Charging

X-rays carry no charge, but at the energies involved, Auger decay of ionized species in a specimen is more probable than radiative decay. High-energy radiation exceeding the ionization potential also generates free electrons which are negligible compared to those produced by electron beams which are charged. Charging of the sample following ionization is an extremely weak possibility when it cannot be guaranteed the ionized electrons leaving the surface or remaining in the sample are adequately balanced from other sources in time. The energy transfer to electrons as a result of ionizing radiation results in separated positive and negative charges which quickly recombine due partly to the long range of the Coulomb force. Insulating films like gate oxides and resists have been observed to charge to a positive or negative potential under X-ray and electron-beam irradiation. Insulating films are eventually neutralized locally by space charge (electrons entering and exiting the surface) at the resist-vacuum interface and Fowler-Nordheim injection from the substrate. The range of the electrons in the film can be affected by the local electric field. The situation is complicated by the presence of holes (positively charged electron vacancies) which are generated along with the secondary electrons, and which may be expected to follow them around. As neutralization proceeds, any initial charge concentration effectively starts to spread out. The final chemical state of the film is reached after neutralization is completed, after all the electrons have eventually slowed down. Usually, excepting X-ray steppers, charging can be further controlled by flood gun or resist thickness or charge dissipation layer.

Maskless lithography

In **maskless lithography**, the radiation that is used to expose a photosensitive emulsion (or photoresist) is not projected from, or transmitted through, a photomask. Instead, most commonly, the radiation is focused to a narrow beam. The beam is then used to directly write the image into the photoresist, one or more pixels at a time. An alternative method, developed by Micronic Laser Systems, is to scan a programmable reflective photomask, which is then imaged onto the photoresist. This has the advantage of higher throughput and flexibility. Both methods are used to define patterns on photomasks.

A key advantage of maskless lithography is the ability to change lithography patterns from one run to the next, without incurring the cost of generating a new photomask. This may prove useful for double patterning.

Forms of maskless lithography

Currently, the main forms of maskless lithography are electron beam and optical. In addition, focused ion beam systems have established an important niche role in failure analysis and defect repair. Finally, systems based on arrays of probe tips have recently been announced.

Electron beam

The most commonly used form of maskless lithography today is electron beam lithography. Its widespread use is due to the wide range of electron beam systems available accessing an equally wide range of electron beam energies (~10 eV to ~100 keV). This is already being used in wafer-level production at eASIC, which uses conventional direct-write electron beam lithography to customize a single via layer for low-cost production of ASICs.

Most maskless lithography systems currently being developed are based on the use of multiple electron beams. The goal is to use the parallel scanning of the beams to speed up the patterning of large areas. However, a fundamental consideration here is to what degree electrons from neighboring beams can disturb one another (from Coulomb repulsion). Since the electrons in parallel beams are traveling equally fast, they will persistently repel one another, while the electron lenses act over only a portion of the electrons' trajectories.

Optical

Direct laser writing is a very popular form of optical maskless lithography, which offers flexibility, ease of use, and cost effectiveness in R&D processing. This equipment offers rapid patterning at sub-micrometre resolutions, and offers a compromise between performance and cost when working with feature sizes of approximately 200nm or greater.

Interference lithography is another form of optical maskless lithography, but is limited to forming periodic patterns only.

For improved image resolution, ultraviolet light, which has a shorter wavelength than visible light, is used to achieve resolution down to around 100 nm. The main optical maskless lithography systems in use today are the ones developed for generating photomasks for the semiconductor and LCD industries.

Focused ion beam

Focused ion beam systems are commonly used today for sputtering away defects or uncovering buried features. The use of ion sputtering must take into account the redeposition of sputtered material.

Probe tip contact

IBM has developed an alternative maskless lithography technique based on atomic force microscopy see here. In addition, Dip Pen Nanolithography is a promising new approach for patterning submicrometre features.

Future of maskless lithography

Maskless lithography is already used for the production of photomasks and in limited wafer-level production. There are some obstacles ahead of its use in high-volume manufacturing. First, there is a wide diversity of maskless techniques. Even within the electron-beam category, there are several vendors (Mapper Lithography, Canon, Advantest) with entirely different architectures and beam energies. Second, throughput targets exceeding 10 wafers per hour still need to be met. Third, the capacity and ability to handle the large data volume (Tb-scale) needs to be developed and demonstrated.

In recent years DARPA and NIST have reduced support for maskless lithography in the U.S .

There is a new European program that will push the insertion of maskless lithography for IC manufacturing at the 32-nm *half-pitch* node in 2009.

Scanning probe lithography

Scanning probe lithography describe a set of lithographic methods, in which a microscopic or nanoscopic stylus is moved mechanically across a surface to form a pattern.

This type of method can be split in two different groups:

> *Constructive* - In which the patterning is done by directly transferring chemical species to the surface (Dip Pen Nanolithography)
> *Destructive* - In which the patterning is done by providing the substrate with energy (Either mechanical, or thermal, photonic, ionic, electronic, Xrays, and so on and so forth) to physically, chemically, electronically deform the substrate's surface. Examples include nanoimprint lithography and local oxidation nanolithography.

Magnetolithography

Magnetolithography (ML) is a method for pattern surfaces. ML based on applying a magnetic field on the substrate using paramagnetic metal masks named "magnetic mask". Magnetic mask which is analog to photomask define the spatial distribution and shape of the applied magnetic field. The second component is ferromagnetic nanoparticles (anlog to photoresist) that are assembled onto the substrate according to the field induced by the magnetic mask.

ML can be used for applying either a positive or negative approach. In the positive approach, the magnetic nanoparticles react chemically or interact via chemical recognition with the substrate. Hence, the magnetic nanoparticles are immobilized at selected locations, where the mask induces a magnetic field, resulting in a patterned substrate. In the negative approach, the magnetic nanoparticles are inert to the substrate. Hence, once they pattern the substrate, they block their binding site on the substrate from reacting with another reacting agent. After the adsorption of the reacting agent, the nanoparticles are removed, resulting in a negatively patterned substrate.

ML is a backside lithography, which has the advantage of ease in producing multilayer with high accuracy of alignment and with the same efficiency for all layers.

Soft lithography

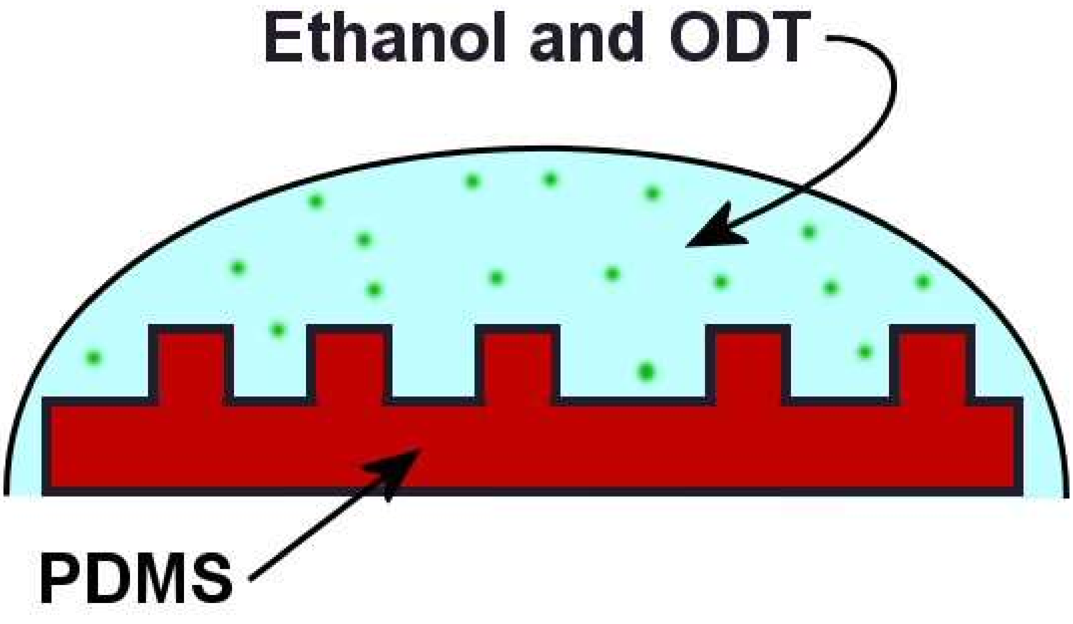


Figure 1 - "Inking" a stamp. PDMS stamp with pattern is placed in Ethanol and ODT solution

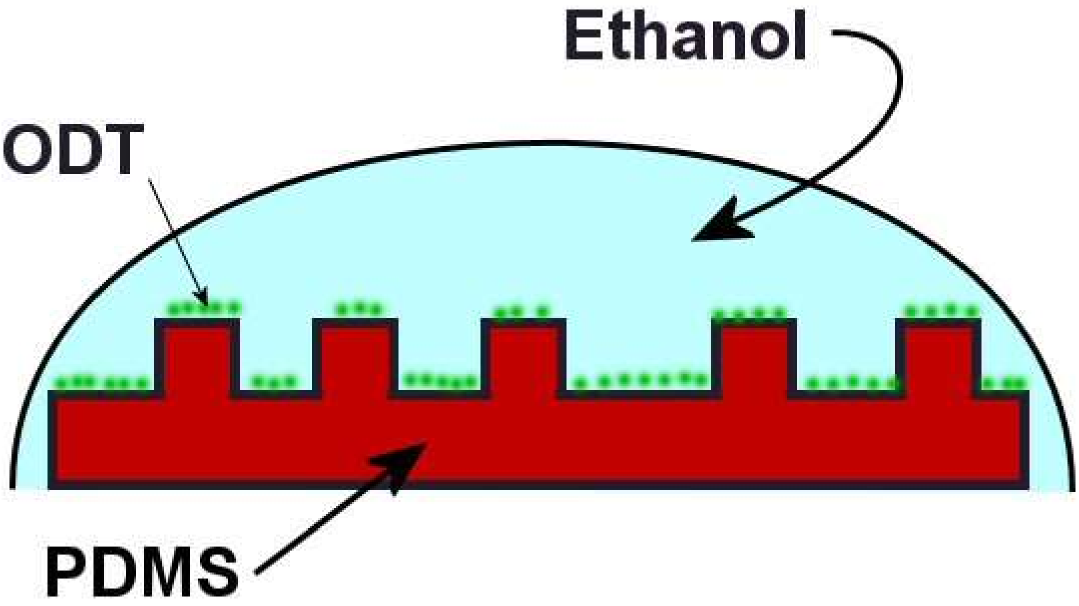


Figure 2 - ODT from the solution settles down onto the PDMS stamp. Stamp now has ODT attached to it which acts as the ink.

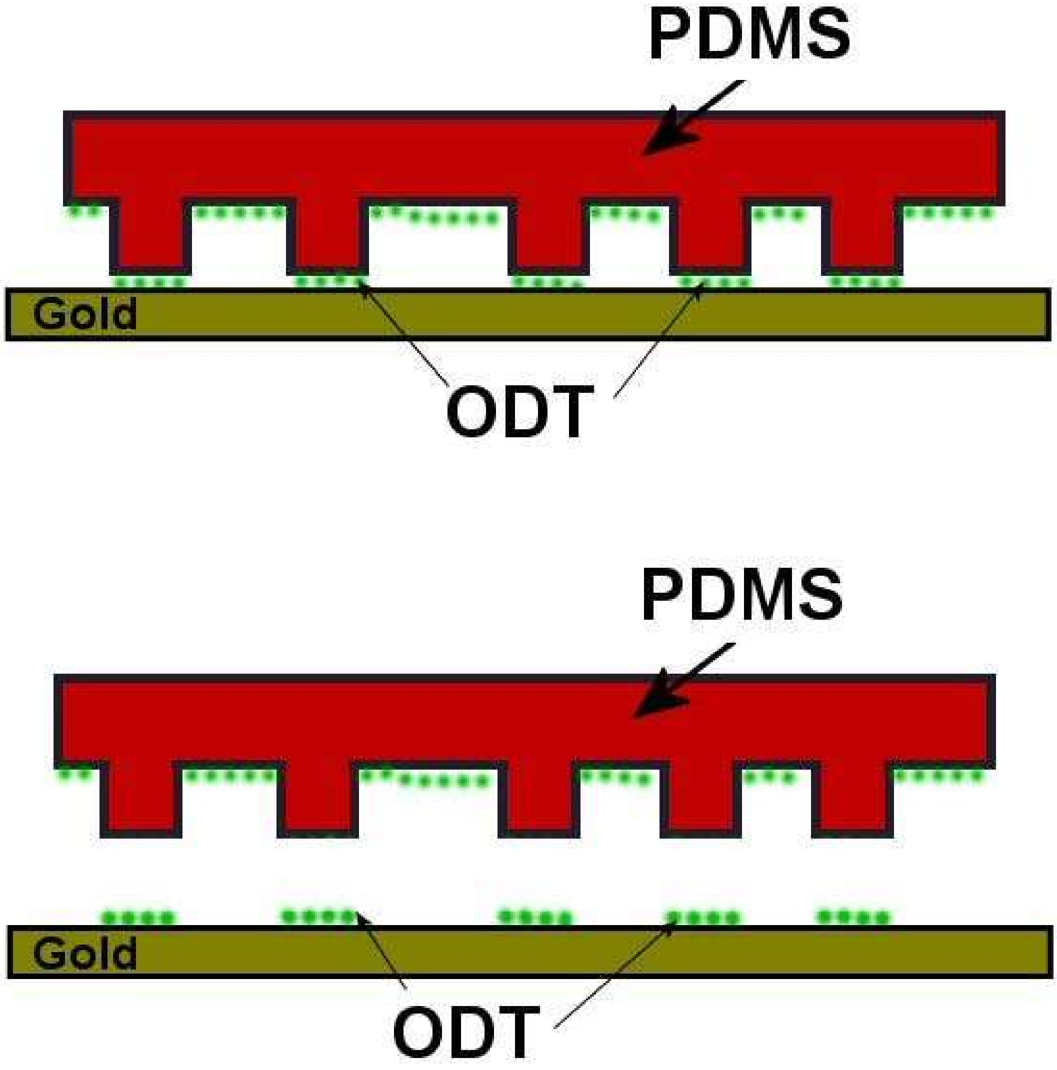


Figure 3 - The PDMS stamp with the ODT is placed on the gold substrate. When the stamp is removed, the ODT in contact with the gold stays stuck to the gold. Thus the pattern from the stamp is transferred to the gold via the ODT "ink."

In technology, **soft lithography** refers to a family of techniques for fabricating or replicating structures using "elastomeric stamps, molds, and conformable photomasks" (in the words of Rogers and Nuzzo, p. 50, as cited in "References"). It is called "soft" because it uses elastomeric materials, most notably PDMS. Soft lithography is generally used to construct features measured on the micrometer to nanometer scale. According to Rogers and Nuzzo (2005), development of soft lithography expanded rapidly during the period 1995 to 2005.

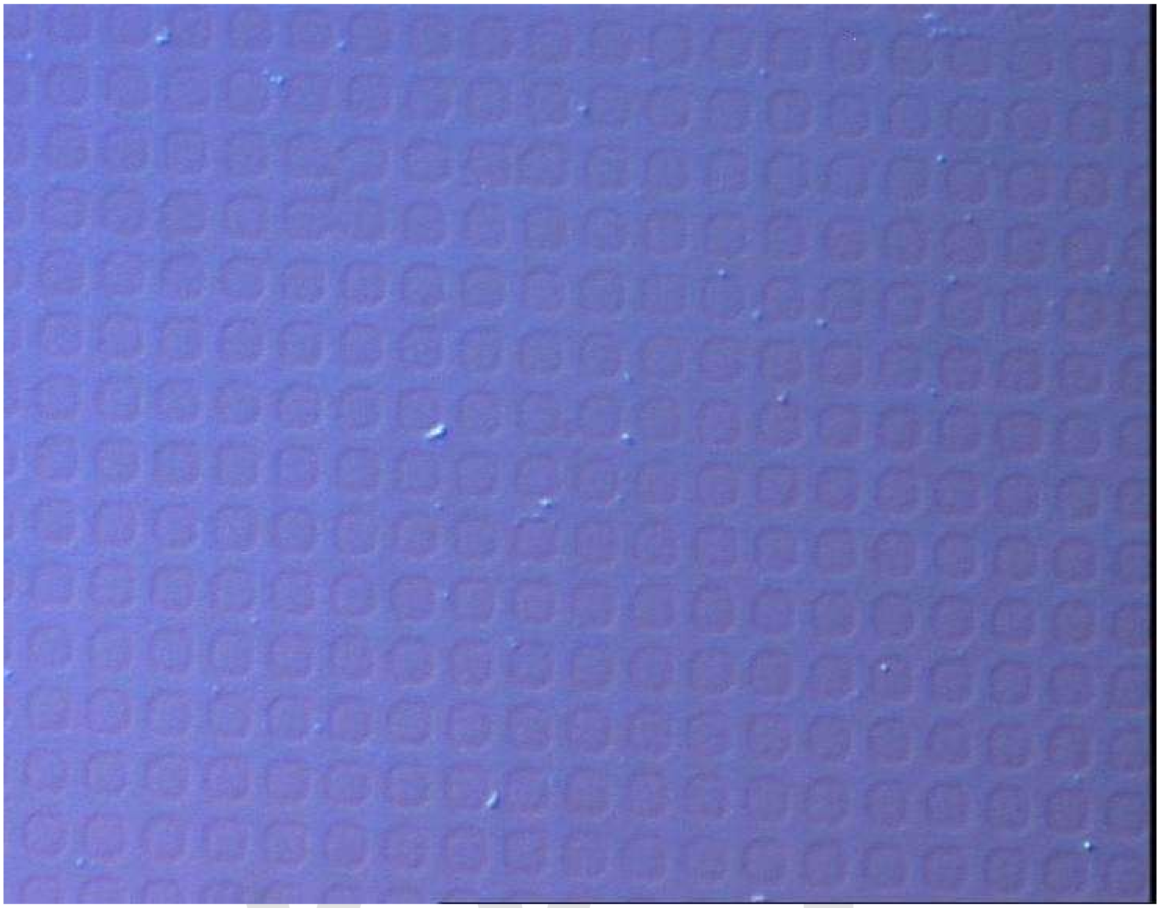
Procedure

Soft lithography refers to a family of techniques that use an elastomer. Polyurethanes, epoxides, and polyimides have been used as liquid prepolymers and are commercially available, but the most common material used in soft lithography is polydimethylsiloxane (PDMS). To produce a pattern it is first necessary to produce a master out of a hard material. Available methods to fabricate the master include photolithography, electron beam lithography, focused ion beam, and polymer masks. Once a master has been produced, a negative in bas-relief is made by casting a mixture of PDMS with crosslinking agent against it and allowing it to harden. Sylgard 184 is a commercial two part PDMS kit that is widely used for many types of soft lithography. The master can be used repeatedly to make many replicas, depending on the durability of the master used. There are size limitations of the features that can be produced, but patterns from nm to mm are routinely obtained. Harder formulations of PDMS are available that can make features of 100 nm when backed with a softer PDMS. PDMS is a useful material because it is optically transparent to ~300 nm, thermally stable to 150 oC, inert to many of the chemicals used to form monolayers, and has desirable physical properties. Its low surface energy allows easy release from templates and surfaces. It contains no solvent to evaporate, and it has low thermal expansion. A number of soft lithographic techniques have been developed for the patterning of materials inside channels of PDMS that do not relate to functionalization of a surface.

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) (From Xia et al.) Patterning by etching at the nanoscale (PENs) One of the soft lithography procedures, Micro contact printing as discussed by Xia and Whitesides, 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 in a bath of inking solution (for example, ODT in ethanol) for a short period of time(Figure 1). The ink molecules then diffuse into the stamp (Figure 2).
5. The inked stamp is brought in contact with the substrate for a certain length of time, allowing ink molecules to transfer onto the substrate surface. The stamp is removed, leaving the desired single-molecule thick pattern on the substrate (Figure 3)
6. Steps 4 and 5 are repeated for each substrate on which the pattern is desired

Advantages

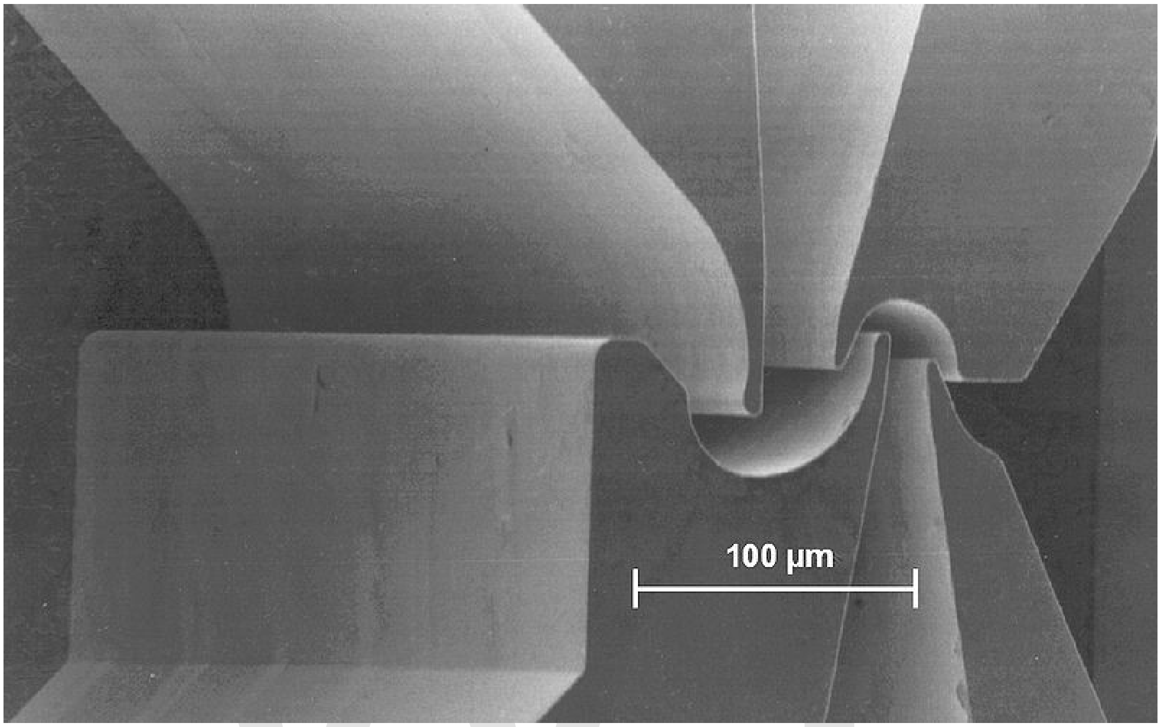


Sarfus image of streptavidin deposited by soft lithography with PDMS stamp.

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 ~100 nm). The resolution depends on the mask used and can reach 6 nm.

LIGA



The X-ray LIGA process was originally developed at the Forschungszentrum Karlsruhe, Germany, to produce nozzles for uranium enrichment.

LIGA is a German acronym for ***Li**thographie, **G**alvanoformung, **A**bformung* (Lithography, Electroplating, and Molding) that describes a fabrication technology used to create high-aspect-ratio microstructures.

Overview

There are two main LIGA-fabrication technologies, **X-Ray LIGA**, which uses X-rays produced by a synchrotron to create high-aspect ratio structures, and **UV LIGA**, a more accessible method which uses ultraviolet light to create structures with relatively low aspect ratios.

The notable characteristics of X-ray LIGA-fabricated structures include:

- high aspect ratios on the order of 100:1
- parallel side walls with a flank angle on the order of 89.95°
- smooth side walls with R_a = 10 nm, suitable for optical mirrors
- structural heights from tens of microns to several millimeters
- structural details on the order of micrometers over distances of centimeters

X-Ray LIGA

X-Ray LIGA is a fabrication process in microtechnology that was developed in the early 1980s by a team under the leadership of Erwin Willy Becker and Wolfgang Ehrfeld at the Institute for Nuclear Process Engineering (*Institut für Kernverfahrenstechnik,* IKVT) at the Karlsruhe Nuclear Research Center, since renamed to the Institute for Microstructure Technology (*Institut für Mikrostrukturtechnik*, IMT) at the Karlsruhe Research Center (*Forschungszentrum Karlsruhe*). LIGA was one of the first major techniques to allow on-demand manufacturing of high-aspect-ratio structures (structures that are much taller than wide) with lateral precision below one micrometer.

In the process, an X-ray sensitive polymer photoresist, typically PMMA, bonded to an electrically conductive substrate, is exposed to parallel beams of high-energy X-rays from a synchrotron radiation source through a mask partly covered with a strong X-ray absorbing material. Chemical removal of exposed (or unexposed) photoresist results in a three-dimensional structure, which can be filled by the electrodeposition of metal. The resist is chemically stripped away to produce a metallic mold insert. The mold insert can be used to produce parts in polymers or ceramics through injection molding.

The LIGA technique's unique value is the precision obtained by the use of deep X-ray lithography (DXRL). The technique enables microstructures with high aspect ratios and high precision to be fabricated in a variety of materials (metals, plastics, and ceramics). Many of its practitioners and users are associated with or are located close to synchrotron facilities.

UV LIGA

UV LIGA utilizes an inexpensive ultraviolet light source, like a mercury lamp, to expose a polymer photoresist, typically SU-8. Because heating and transmittance are not an issue in optical masks, a simple chromium mask can be substituted for the technically sophisticated X-ray mask. These reductions in complexity make UV LIGA much cheaper and more accessible than its X-ray counterpart. However, UV LIGA is not as effective at producing precision molds and is thus used when cost must be kept low and very high aspect ratios are not required.

Process details

The LIGA-fabrication process is composed of exposure (a), development (b), electroforming (c), stripping (d), and replication (e).

Mask

X-ray masks are composed of a transparent, low-Z carrier, a patterned high-Z absorber, and a metallic ring for alignment and heat removal. Due to extreme temperature variations induced by the X-ray exposure, carriers are fabricated from materials with high thermal conductivity to reduce thermal gradients. Currently, vitreous carbon and graphite are considered the best material, as their use significantly reduces side-wall roughness. Silicon, silicon nitride, titanium, and diamond are also in use as carrier substrates but not preferred, as the required thin membranes are comparatively fragile and titanium masks tend to round sharp features due to edge fluorescence. Absorbers are gold, nickel, copper, tin, lead, and other x-ray absorbing metals.

Masks can be fabricated in several fashions. The most accurate and expensive masks are those created by electron beam lithography, which provides resolutions as fine as 0.1 µm in resist 4 µm thick and 3 µm features in resist 20 µm thick. An intermediate method is the plated photomask which provides 3 µm resolution and can be outsourced at a cost on the order of $1000 per mask. The least expensive method is a direct photomask, which provides 15 µm resolution in resist 80 µm thick. In summary, masks can cost between $1000 and $20,000 and take between two weeks and three months for delivery. Due to the small size of the market, each LIGA group typically has its own mask-making capability. Future trends in mask creation include larger formats, from a diameter of 100 mm to 150 mm, and smaller feature sizes.

Substrate

The starting material is a flat substrate, such as a silicon wafer or a polished disc of beryllium, copper, titanium, or other material. The substrate, if not already electrically conductive, is covered with a conductive plating base, typically through sputtering or evaporation.

The fabrication of high-aspect-ratio structures requires the use of a photoresist able to form a mold with vertical sidewalls. Thus the photoresist must have a high selectivity and be relatively free from stress when applied in thick layers. The typical choice, poly(methyl methacrylate) (PMMA) is applied to the substrate by a glue-down process in which a precast, high-molecular-weight sheet of PMMA is attached to the plating base on the substrate. The applied photoresist is then milled down to the precise height by a fly cutter prior to pattern transfer by X-ray exposure. Because the layer must be relatively free from stress, this glue-down process is preferred over alternative methods such as casting. Further, the cutting of the PMMA sheet by the fly cutter requires specific operating conditions and tools to avoid introducing any stress and crazing of the photoresist.

Exposure

A key enabling technology of LIGA is the synchrotron, capable of emitting high-power, highly collimated X-rays. This high collimation permits relatively large distances between the mask and the substrate without the penumbral blurring that occurs from other X-ray sources. In the electron storage ring or synchrotron, a magnetic field constrains electrons to follow a circular path and the radial acceleration of the electrons causes electromagnetic radiation to be emitted forward. The radiation is thus strongly collimated in the forward direction and can be assumed to be parallel for lithographic purposes. Because of the much higher flux of usable collimated X-rays, shorter exposure times become possible. Photon energies for a LIGA exposure are approximately distributed between 2.5 and 15 keV.

Unlike optical lithography, there are multiple exposure limits, identified as the top dose, bottom dose, and critical dose, whose values must be determined experimentally for a proper exposure. The exposure must be sufficient to meet the requirements of the bottom dose, the exposure under which a photoresist residue will remain, and the top dose, the exposure over which the photoresist will foam. The critical dose is the exposure at which unexposed resist begins to be attacked. Due to the insensitivity of PMMA, a typical exposure time for a 500 µm thick PMMA is six hours. During exposure, secondary radiation effects such as Fresnel diffraction, mask and substrate fluorescence, and the generation of Auger electrons and photoelectrons can lead to overexposure.

During exposure the X-ray mask the mask and the mask holder are heated directly by X-ray absorption and cooled by forced convection from nitrogen jets. Temperature rise in PMMA resist is mainly from heat conducted from the substrate backward into the resist and from the mask plate through the inner cavity air forward to the resist, with X-ray absorption being tertiary. Thermal effects include chemistry variations due to resist heating and geometry-dependent mask deformation.

Development

For high-aspect-ratio structures the resist-developer system is required to have a ratio of dissolution rates in the exposed and unexposed areas of 1000:1. The standard, empirically optimized developer is a mixture of tetrahydro-1,4-oxazine (20 %), 2-aminoethanol-1 (5 %), 2-(2-butoxyethoxy)ethanol (60 %), and water (15 %). This developer provides the required ratio of dissolution rates and reduces stress-related cracking from swelling in comparison to conventional PMMA developers. After development, the substrate is rinsed with deionized water and dried either in a vacuum or by spinning. At this stage, the PMMA structures can be released as the final product (e.g., optical components) or can be used as molds for subsequent metal deposition.

Electroplating

In the electroplating step, nickel, copper, or gold is plated upward from the metalized substrate into the voids left by the removed photoresist. Taking place in an electrolytic cell, the current density, temperature, and solution are carefully controlled to ensure proper plating. In the case of nickel deposition from $NiCl_2$ in a KCl solution, Ni is deposited on the cathode (metalized substrate) and Cl_2 evolves at the anode. Difficulties associated with plating into PMMA molds include voids, where hydrogen bubbles nucleate on contaminates; chemical incompatibility, where the plating solution attacks the photoresist; and mechanical incompatibility, where film stress causes the plated layer to lose adhesion. These difficulties can be overcome through the empirical optimization of the plating chemistry and environment for a given layout.

Stripping

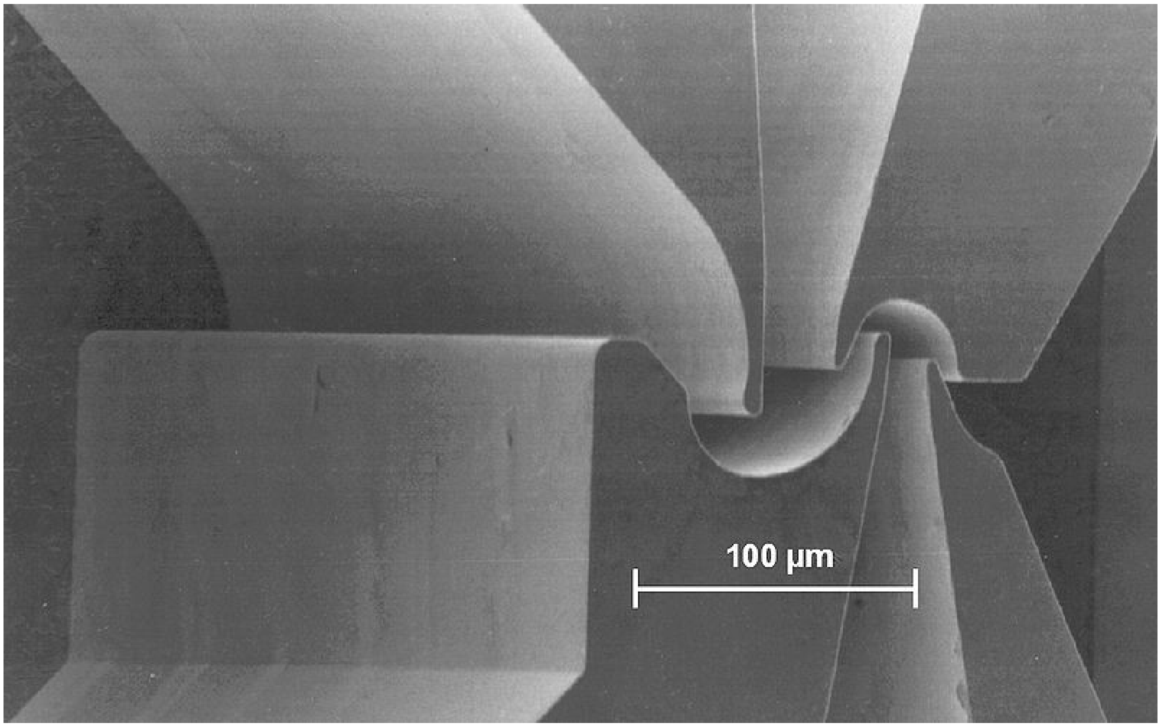
After exposure, development, and electroplating, the resist is stripped. One method for removing the remaining PMMA is to flood expose the substrate and use the developing solution to cleanly remove the resist. Alternatively, chemical solvents can be used. Stripping of a thick resist chemically is a lengthy process, taking two to three hours in acetone at room temperature. In multilayer structures, it is common practice to protect metal layers against corrosion by backfilling the structure with a polymer-based encapsulant. At this stage, metal structures can be left on the substrate (e.g., microwave circuitry) or released as the final product (e.g., gears).

Replication

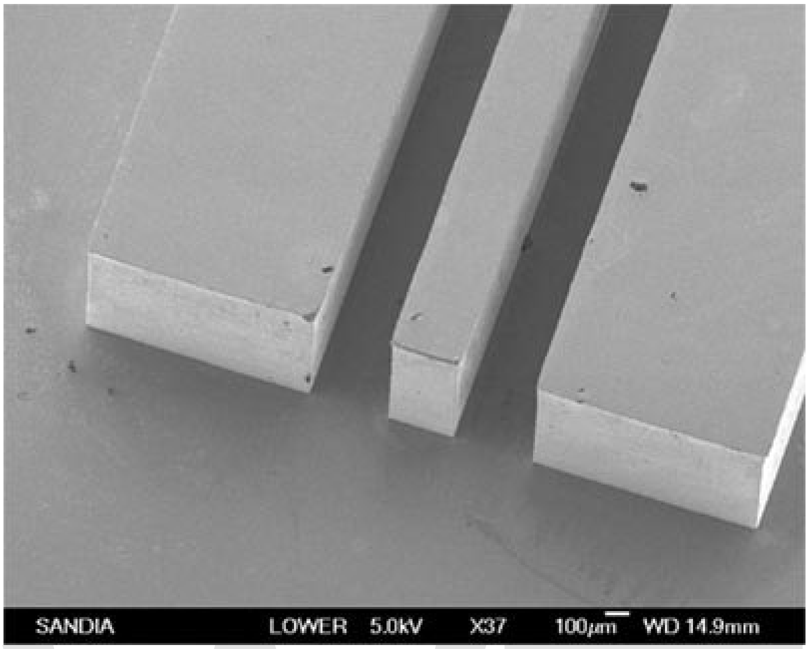
After stripping, the released metallic components can be used for mass replication through standard means of replication such as stamping or injection molding.

Gallery

Below is a gallery of LIGA-fabricated structures arranged by date.



A nozzle for uranium enrichment.



A 517 µm tall copper coplanar waveguide.

Patterning by etching at the nanoscale

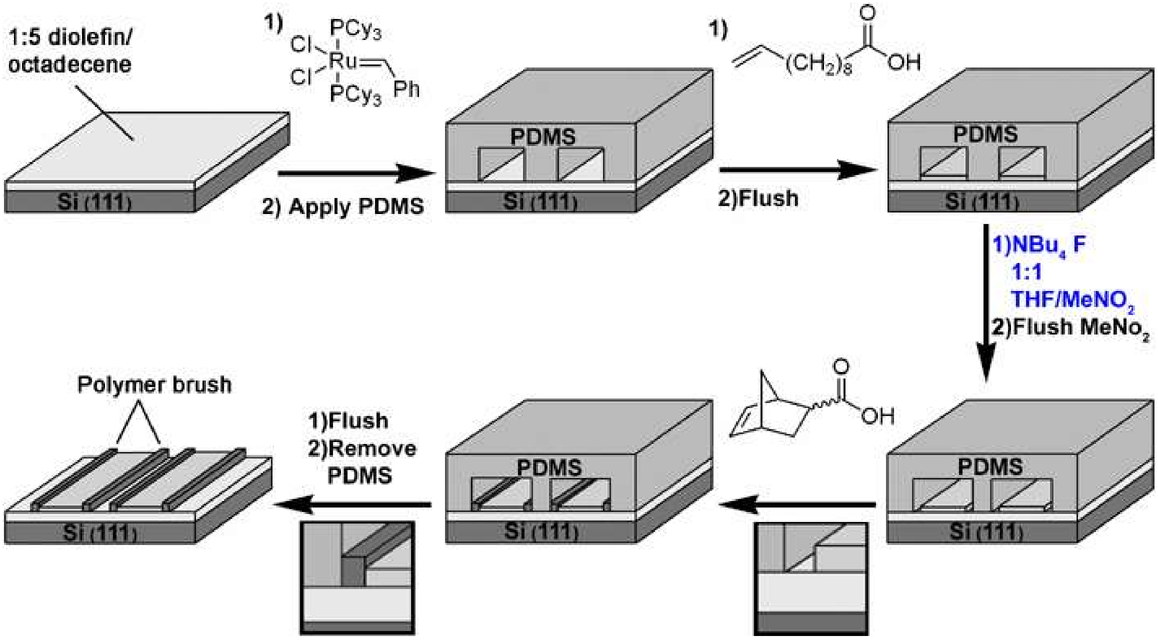


Figure 1 - Example of a procedure using ammonium fluoride as an etchant and polymer brushes for visulaisation

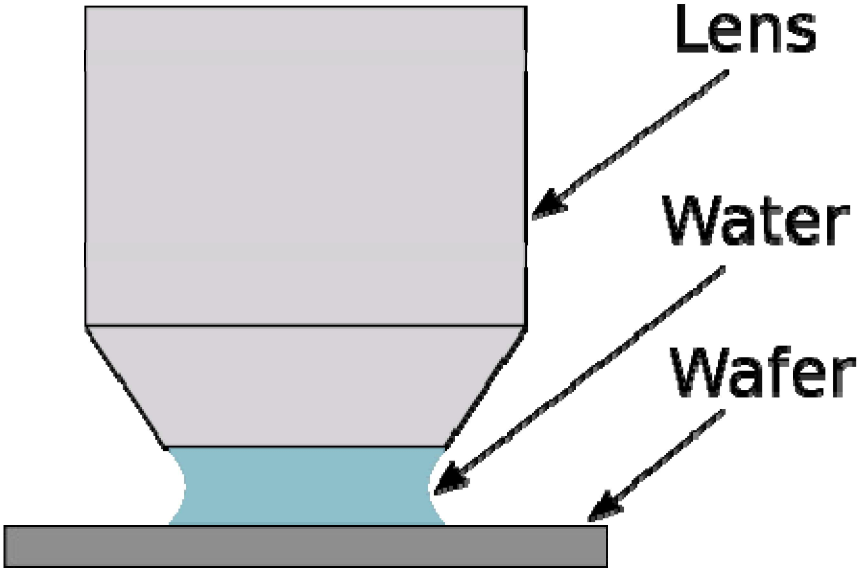
Patterning by Etching at the nanoscale (PENs) is a soft lithographic technique in which the bonds in the PDMS matrix are broken to controlably etch PDMS (ie dissolve) at a slow rate along the outside of a PDMS channel formed with a patterned PDMS stamp applied to a surface. The channel in the stamp can be enlarged in the order of tens of nanometers to several micrometres. Exposing a fresh area of a surface that can be reacted with.

Summary

PDMS contains polymer chains of silicon-oxygen bonds, these bonds can be broken by fluoride containing species, in the same way that silicon wafers are prepared by etching with hydrofluoric acid, ammonium fluoride and related compounds. By placing a PDMS stamp that contains a channel that can be externally filled on to a surface, that surface can be functionalised in the area of the channel. By then running an etching solution through the channel, part of the PDMS will be removed. Exposing a fresh area of the surface. This can then be functionaliesd by appropriate chemistry. The width of feature produced is controlled by etchant and time.

To apply this technique for the production of small patterned features it is necessary that the surface can be reacted to passivate it in the area exposed by the channel, followed by etching and then reacted in away that will only occur in the newly exposed area.

Immersion lithography



In immersion lithography, light travels down through a system of lenses and then a pool of water before reaching the photoresist on top of the wafer.

Immersion lithography is a nanolithography resolution enhancement technique that replaces the usual air gap between the final lens and the wafer surface with a liquid medium that has a refractive index greater than one. The resolution is increased by a factor equal to the refractive index of the liquid. Current immersion lithography tools use highly purified water for this liquid, achieving feature sizes below 45 nanometers. ASML, Nikon and Canon are currently the only manufacturers of immersion lithography systems. An enhancement is HydroLith immersion technology which allows a "measure dry, expose wet" process.

Benefits of immersion lithography

The ability to resolve features in optical lithography is directly related to the numerical aperture of the imaging equipment, the numerical aperture being the sine of the maximum refraction angle multiplied by the refractive index of the medium through which the light travels. The lenses in the highest resolution "dry" photolithography scanners focus light in a cone whose boundary is nearly parallel to the wafer surface. As it is impossible to increase resolution by further refraction, additional resolution is obtained by inserting an immersion medium with a higher index of refraction between the lens and the wafer. The blurriness is reduced by a factor equal to the refractive index of the medium. For example, for water immersion using ultraviolet light at 193 nm wavelength, the index of refraction is 1.44.

The resolution enhancement from immersion lithography is about 30-40% (depending on materials used). The depth of focus, or tolerance in wafer topography flatness, is also ~2x better than a corresponding "dry" tool at the same resolution.

The successful emergence of immersion lithography comes not just from its ability to extend resolution and depth of focus, but also from its timely introduction to the industry (e.g., IBM, AMD) between 65 nm and 45 nm nodes.

Intel's 32nm process uses second-generation high-k, metal gate technology, but this will be the first time Intel has deployed immersion lithography.

Manufacturing issues

The main obstacle to adoption of immersion lithography systems has been defects and other possible sources of yield loss. Early studies focused on the elimination of bubbles in the immersion fluid, temperature and pressure variations in the immersion fluid, and immersion fluid absorption by the photoresist. Degassing the fluid, carefully constraining the fluid thermodynamics and carefully treating the top layer of photoresist have been key to the implementation of immersion lithography. Defects intrinsic to immersion lithography have been identified. Reducing particle generation due to the water dispensing unit was found to reduce the incidence of defects. Water also has been shown to extract acid from photoresist. Specifically, photoacid generators (PAGs) are extracted into the water, which produce acid upon radiation exposure. This must be managed to ensure the lens is not corroded by the acid or contaminated by the extracted agents, and the photoresist is not chemically altered to the point of being defective. Still, since diffusion of contaminants is expected to be much slower in water than in air or vacuum, consideration of optics contamination actually favors immersion lithography. Water-soaked photoresist also has been demonstrated to produce very satisfactory images.

In addition, 193 nm light has been known to ionize water, producing solvated electrons, which may spread and react with the photoresist, affecting the resolution performance.

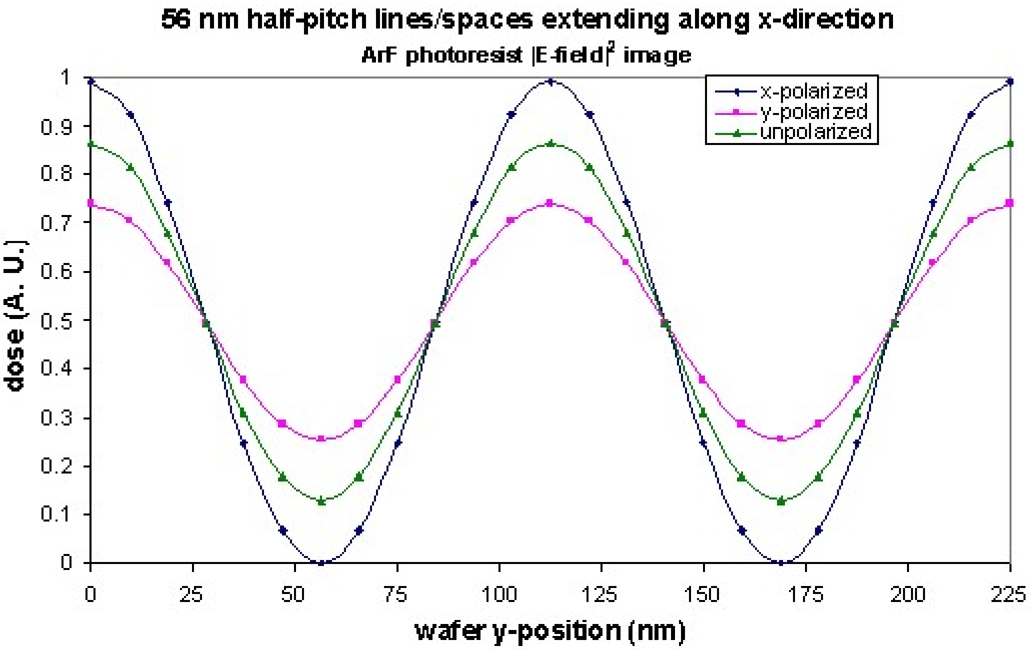
The above defect concerns have led to considerations of using a topcoat layer directly on top of the photoresist. This topcoat would serve as a barrier for chemical diffusion between the liquid medium and the photoresist. In addition, the interface between the liquid and the topcoat would be optimized for watermark reduction. At the same time, defects from topcoat use should be avoided.

As scanning speeds typically approach 500 mm/s for high-volume manufacturing, the actual resist-water contact time in any given exposure area is minimal. Hence the main concerns for defects are water left behind (watermarks) and loss of resist-water adhesion (air gap). The hydrophobicity of the surface and the water delivery/removal method are therefore the key areas to address. Other areas where defects may be enhanced are at the wafer edge, where the water has to do an "about-face" (reverse motion). It is important for the water not to pick up defects from the wafer backside.

Generally, implementation into manufacturing is only considered when defect yields reach a mature level, e.g., comparable to dry lithography levels.

Future of immersion lithography

As of 2007, many companies, including IBM, UMC, Toshiba, and TI are ramping for the 45 nm node using immersion lithography. AMD's Fab 36 is already equipped for using immersion lithography for its 65 nm, 45 nm and 32 nm node technologies. AMD has also made preparations for advanced design for manufacturability (DFM), including layout regularity and double patterning at the 22 nm node, using immersion lithography. For the 32 nm node in 2009, Intel will begin using immersion lithography as well. Intel has confirmed that since EUV will not be available, it will extend 193 nm immersion lithography to the 22 nm node and 15 nm node. Intel has already outlined a path to use 193 nm immersion lithography down to 11 nm node. IBM has also stated that it will be using immersion lithography for the 22 nm node, since no other alternative is available at this time.



Polarization effects in immersion lithography. For pitches where immersion lithography is relevant, the polarization will affect the intensity inside the photoresist. This example is for 56 nm half-pitch.

Enhancements necessary to extend the technology beyond the 32 nm node are currently being investigated. Such enhancements include the use of higher refractive-index materials in the final lens, immersion fluid, and photoresist, in order to improve the resolution with single patterning. Currently, the most promising high-index lens material is lutetium aluminum garnet, with a refractive index of 2.14. High-index immersion fluids are approaching refractive index values of 1.7. These new developments allow the optical resolution to approach ~30 nm. However, it is expected that at some point below 40 nm, current photoresists will limit further scaling. Polarization effects due to high angles of interference in the photoresist also have to be considered as features approach 40 nm. Hence, new photoresists will need to be developed for sub-40 nm applications.

On the other hand, double patterning has received interest recently since it can potentially increase the half-pitch resolution by a factor of 2. This could allow the use of immersion lithography tools beyond the 32 nm node, potentially to the 16 nm node. While double patterning improves pitch resolution, it must rely on non-lithographic methods, such as trimming, to actually reduce the feature size, possibly by as much as 50%.