

**PREPARATION**

Top-Down and Bottom-Up approaches of nanomaterial (nano particles, nanoclusters and quantum dots) synthesis: to-down techniques: photolithography, other optical lithography (EUV, x-ray, LIL), Particle-beam lithographies (e-beam, FIB, shadow mask evaporation), probe lithographies, bottom-up techniques: self-assembly, self-assembled monolayers, directed assembly, layer-by-layer assembly. Pattern replication techniques: soft lithography, nano imprint lithography. Pattern transfer and enhancement techniques: dry etching, wet etching, pattern growth techniques (polymerization, directed assembly)

**Top-Down approaches and Bottom- Up approaches**

There are plenty of methods to synthesis nano materials. These methods are grouped into two categories namely Top-Down and Bottom-Up techniques. The techniques are classified based on the phase of the starting material. In the Top-down class of techniques, the starting material is in solid state, whereas in Bottom-Up techniques the starting material is either in gaseous state or in liquid state.

Top-down approach refers to a subtractive process in which a bulk starting material is divided into smaller ones of nanosize. Bottom-up approach refers to an additive process that starts with precursor atoms (or) molecules which combine to form nanosized structure. In bottom-up approach, nanostructures are built atom-by-atom or molecule-by-molecule. Depending on the requirement we have to select an appropriate method for preparation of nano materials.

**Top-Down approaches**

Few methods are listed

- ✓ Mechanical grinding (Ball Milling)
- ✓ Lithography
- ✓ Etching
- ✓ Erosion

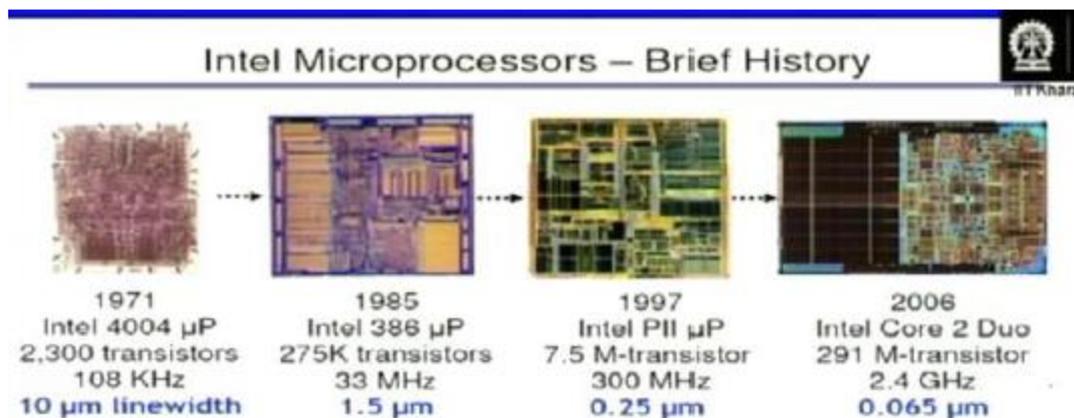
**Bottom- Up approaches**

Few methods are listed

- ✓ Sol gel method
- ✓ Chemical Vapour Deposition
- ✓ Physical Vapour Deposition
- ✓ Electrochemical deposition
- ✓ Hydrothermal method
- ✓ Atomic layer deposition

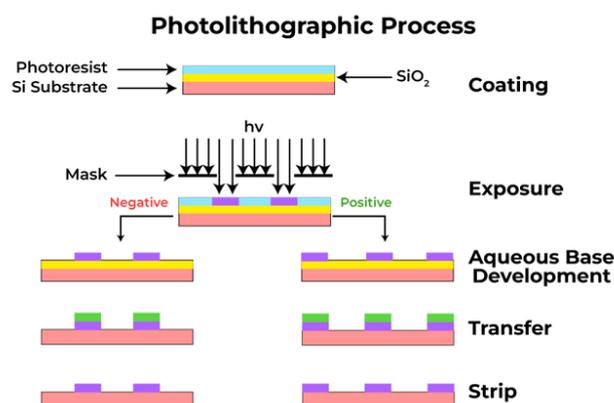
## Photolithography

Photolithography is the main motive force for the tremendous advancement in the field of microelectronics. These are some numbers you may be interested, transistor was first invented in 1947, the first IC or the integrated circuit was built in 1960; at that time the line width; it is the width of P or the N type domains was roughly five microns. So, first IBM PC was developed in 1981 with a 16 kilobyte memory, sounds childish now and a 4.77 megahertz clock speed. For a 40 GB D-RAM, around 1997, it was huge the line width was 350 nanometer; and as we have talked in one of our previous lecture, the line width is roughly around 30 to 35 nanometer for core I5 processors of Intel as of 2011. Now, closer is the packing, better is the performance of the circuit, higher number of transistors you can put so faster other things.



By line width, we are talking about the widths of the P type and N type domains. So, each one of the interfaces of the P type domain and N type domain acts as a transistor. We create these type of arrays of P and N type domains on a silicon wafer, which is the basic building block for the microelectronic industry; as of today is achieved or can be achieved by the method of photolithography. So, this advancement of how many transistors you can place inexpensively on an integrated circuit has given rise to the now famous Moore's law, which says that the number of transistors that can be placed in expensively on an integrated circuit doubles approximately every two years.

- ✓ Photolithography or UV lithography is a method of fabrication of thin film patterns. An optical mask is irradiated with UV light to transfer the existing geometric pattern over the optical mask to a substrate via a light-sensitive chemical process.
- ✓ A single iteration of photolithography combines several steps in sequence. Modern cleanrooms use automated, robotic wafer track systems to coordinate the process.
- ✓ Wafer is a disc like material, which can be few hundred micron to about a millimeter thick. Now, you may also know that silicon is a crystalline material.
- ✓ As soon as a silicon freshly prepared silicon is exposed to atmosphere, which contains lot of oxygen, which is amongst oxygen and nitrogen more reactive species; that is immediately a surface reaction take place and a very thin oxide layer or many times it is written as  $\text{SiO}_x$ , (because this can be non-stoichiometric oxides also) form. This is known as native oxide layer and it has a thickness of 1.5 to 2 nm.
- ✓ Depending on the requirement we can choose either P type doped silicon or N type doped silicon. So let us take a P type doped silicon and it contains a thin oxide layer. Now our aim is to create a N type domains on this P type doped silicon on regular domains so that we will get PN junctions. So, you have to cover parts of the wafer with something, so that the N type doping, the chemical which you are using for the N type doping, can have access to the wafer surface only at certain preferred or preferential locations and not everywhere. Finally IC chip will be ready.



The basic steps are follows

### **(a) Cleaning**

If organic or inorganic contaminations are present on the wafer surface, they are usually removed by wet chemical treatment, e.g. the RCA clean procedure based on solutions containing hydrogen peroxide. Other solutions made with trichloroethylene, acetone or methanol can also be used to clean.

### **(b) Preparation**

The wafer is initially heated to a temperature sufficient to drive off any moisture that may be present on the wafer surface, 150 °C for ten minutes is sufficient. 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 surface layer of silicon dioxide on the wafer reacts with HMDS to form tri-methylated silicon-dioxide, a highly water repellent layer. 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.

### **(c) Photo resist application**

The wafer is covered with photoresist layer 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. 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.

PR is classified into positive PR and negative PR. Positive PR with mask (contains transparent and opaque areas) on irradiation with UV light, the photo resist layer will be degraded on the transparent areas of the photo resist over the opaque areas and becomes soluble in the developer solution and thus we get a pattern exactly equal to that of the mask.

### **(d) Photo mask**

A Photo mask which has required design was placed on the top of this photo resist layer. The photo mask contains some opaque domains and some transparent domains.

### **(e) Exposure and developing.**

The areas of the photo resist layer, which fall below the transparent domain, will undergo some change in their optical properties or will undergo some change due to their exposure to UV light. You have

domains corresponding to the design of the mask and which has been subjected to UV light. So, essentially you create your original pattern on the mask and that preferentially gets transferred onto the photo resist layer. Then the mask is removed and then you apply a different thinners or different chemicals to etch; first of all to resist layer and then you also etch the oxide layer. Only one of the PR layer depending on the type which we have used will be removed by the thinner and then the oxide layer. Then by diffusion reaction N type dope chemicals were deposited on the exposed areas.

#### (f) **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. Use of 1-Methyl-2-pyrrolidone (NMP) solvent for photoresist is another method used to remove an image. When the resist has been dissolved, the solvent can be removed by heating to 80 °C without leaving any residue.

#### **Light source**

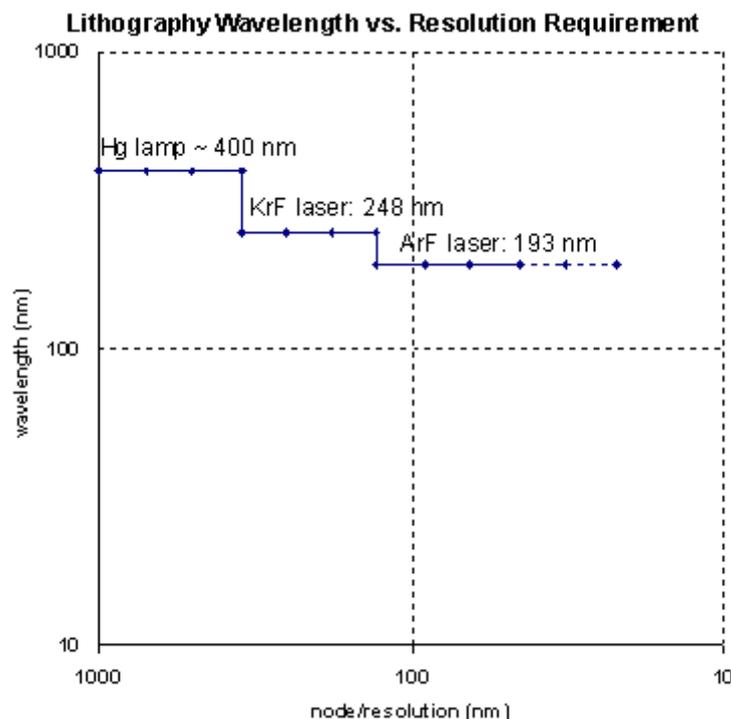
Historically, photolithography has used ultraviolet light from gas-discharge lamps using mercury, sometimes in combination with noble gases such as xenon. These lamps produce light across a broad spectrum with several strong peaks in the ultraviolet range. This spectrum is filtered to select a single spectral line. From the early 1960s through the mid-1980s, Hg lamps had been used in lithography for their spectral lines at 436 nm ("g-line"), 405 nm ("h-line") and 365 nm ("i-line"). However, with the semiconductor industry's need for both higher resolution (to produce denser and faster chips) and higher throughput (for lower costs), the lamp-based lithography tools were no longer able to meet the industry's requirements.

This challenge was overcome when in a pioneering development in 1982, excimer laser lithography was proposed and demonstrated at I.B.M. by Kanti Jain, and now excimer laser lithography machines (steppers and scanners) are the primary tools used worldwide in microelectronics production. With phenomenal advances made in tool technology in the last two decades, it is the semiconductor industry view that excimer laser lithography has been a crucial factor in the continued advance of Moore's Law, enabling minimum features sizes in chip manufacturing to shrink from 0.5 micrometer in 1990 to 45 nanometers and below in 2010. This trend is expected to continue into this decade for even denser chips, with minimum features approaching 10 nanometers. From an even broader scientific and technological perspective, in the 50-year history of the laser since its first demonstration in 1960, the invention and development of excimer laser lithography has been highlighted as one of the major milestones.

The commonly used deep ultraviolet excimer lasers in lithography systems are the krypton fluoride laser at 248 nm wavelength and the argon fluoride laser at 193 nm wavelength. Generally, an

excimer laser is designed to operate with a specific gas mixture; therefore, 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, when exposed to photons with energy greater than the band gap, release free electrons and holes which subsequently cause adverse charging.

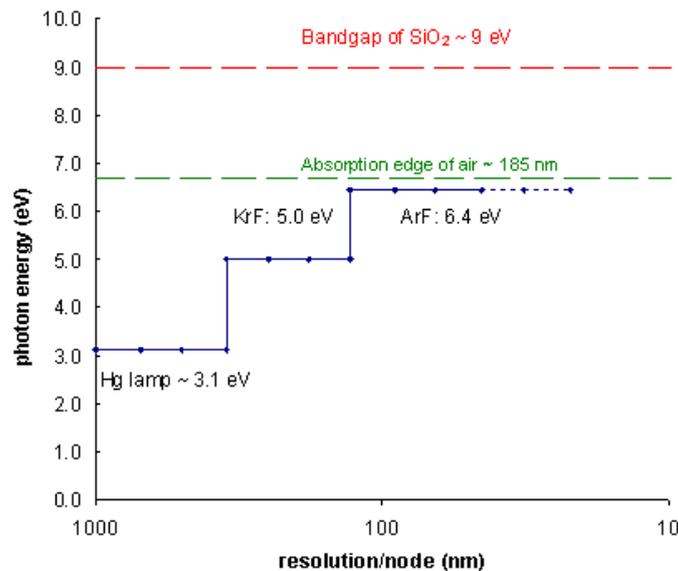
Optical lithography has been extended to feature sizes below 50 nm using the 193 nm ArF excimer laser and liquid immersion techniques. Also termed immersion lithography, this enables the use of optics with numerical apertures exceeding 1.0. The liquid used is typically ultra-pure, deionised water, which 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.



Experimental tools using the 157 nm wavelength from the F<sub>2</sub> excimer laser in a manner similar to current exposure systems have been built. These were once targeted to succeed 193 nm lithography 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 excimer laser lithography 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.

UV excimer lasers have been demonstrated to about 126 nm (for Ar<sub>2</sub>\*). Excimer lasers are generally preferred to more than the mercury arc lamps because they have a higher resolution. Mercury arc lamps are designed to maintain a steady DC current of 50 to 150 Volts, however the resolution is not optimal. Excimer lasers are gas-based light systems that are usually filled with inert and halide gases (Kr, Ar, Xe, F<sub>2</sub> and Cl<sub>2</sub>) that are charged by an electric field. The faster the frequency the greater the resolution of the image. KrF lasers are able to function at a frequency of 4 kHz which is why they are so optimal. In addition to running at a higher frequency, excimer lasers are compatible with more advanced machines than mercury arc lamps are. They are also able to operate from greater distances (up to 25 meters) and are able to maintain their accuracy with a series of mirrors and antireflective-coated lenses. By setting up multiple lasers and mirrors, the amount of energy loss is minimized, also since the lenses are coated with antireflective material, the light intensity remains relatively the same from when it left the laser to when it hits the wafer.



Lasers have been used to indirectly generate non-coherent extreme UV (EUV) light at 13.5 nm for extreme ultraviolet lithography. The EUV light is not emitted by the laser, but rather by a tin or xenon plasma which is excited by an excimer laser. Fabrication of feature sizes of 10 nm has been demonstrated in production environments, but not yet at rates needed for commercialization. However, this is expected by 2016. This technique does not require a synchrotron and EUV sources, as noted, do not produce coherent light. However vacuum systems and a number of novel technologies (including much higher EUV energies than are now produced) are needed to work with UV at the edge of the X-ray spectrum (which begins at 10 nm).

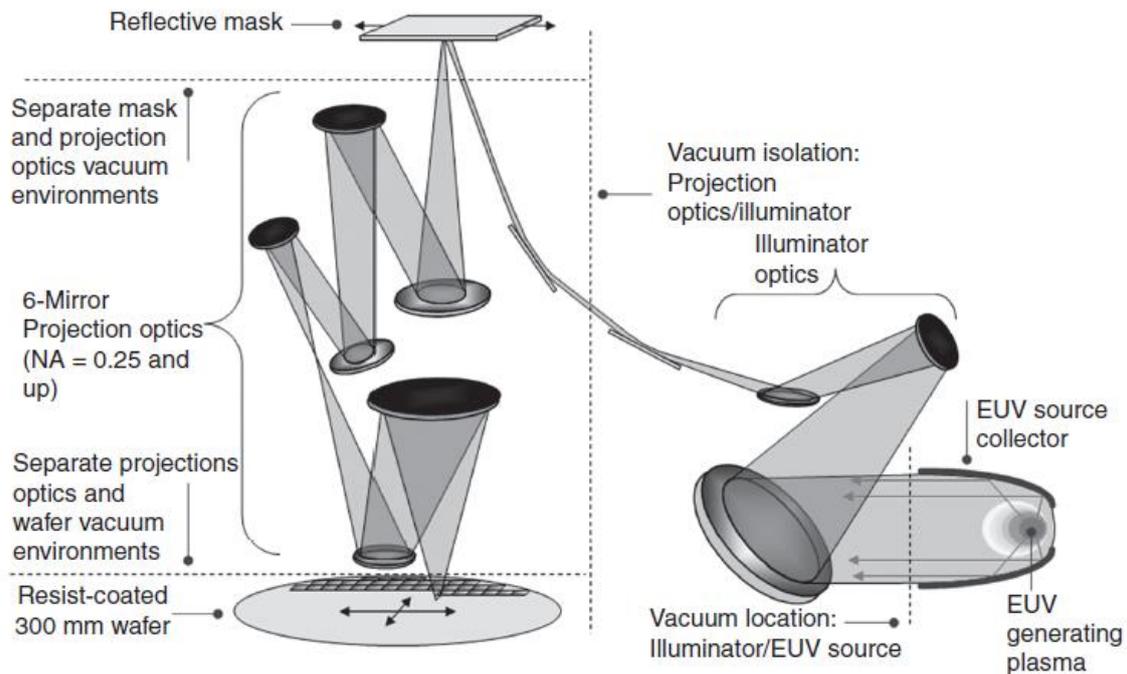
An option, especially if and when wavelengths continue to decrease to extreme UV or X-ray, is the free-electron laser (or one might say xaser for an X-ray device). These can produce high quality beams at arbitrary wavelengths.

## **EUV lithography**

**Extreme ultraviolet lithography** (also known as EUV or EUVL) is a next-generation lithography technology using an extreme ultraviolet (EUV) wavelength, currently expected to be 13.5 nm. EUV is currently being developed for possible future use below 32 nm pitch resolution, sometimes referred to as the 7 nm node, in 2018–19. Figure below shows a schematic of an EUV lithography exposure system. EUVL is a significant departure from the deep ultraviolet lithography standard. All matter absorbs EUV radiation. Hence, EUV lithography requires a vacuum. All optical elements, including the photomask, must use defect-free Mo/Si multilayers that act to reflect light by means of interlayer interference; any one of these mirrors absorb around 30% of the incident light. Multilayer mirror is prepared by using a series of paired thin layers of high and low atomic number (Z) materials. For example Mo/Si. Such a reflector is also called Bragg reflector or more commonly multilayer (ML) reflector.

Current EUVL systems contain at least two condenser multilayer mirrors, six projection multilayer mirrors and a multilayer object (mask). Since the optics already absorbs 96% of the EUV light, the ideal EUV source will need to be much brighter than its predecessors. 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 high-energy ions and other debris. This damage has precluded EUV light sources from success.

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 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



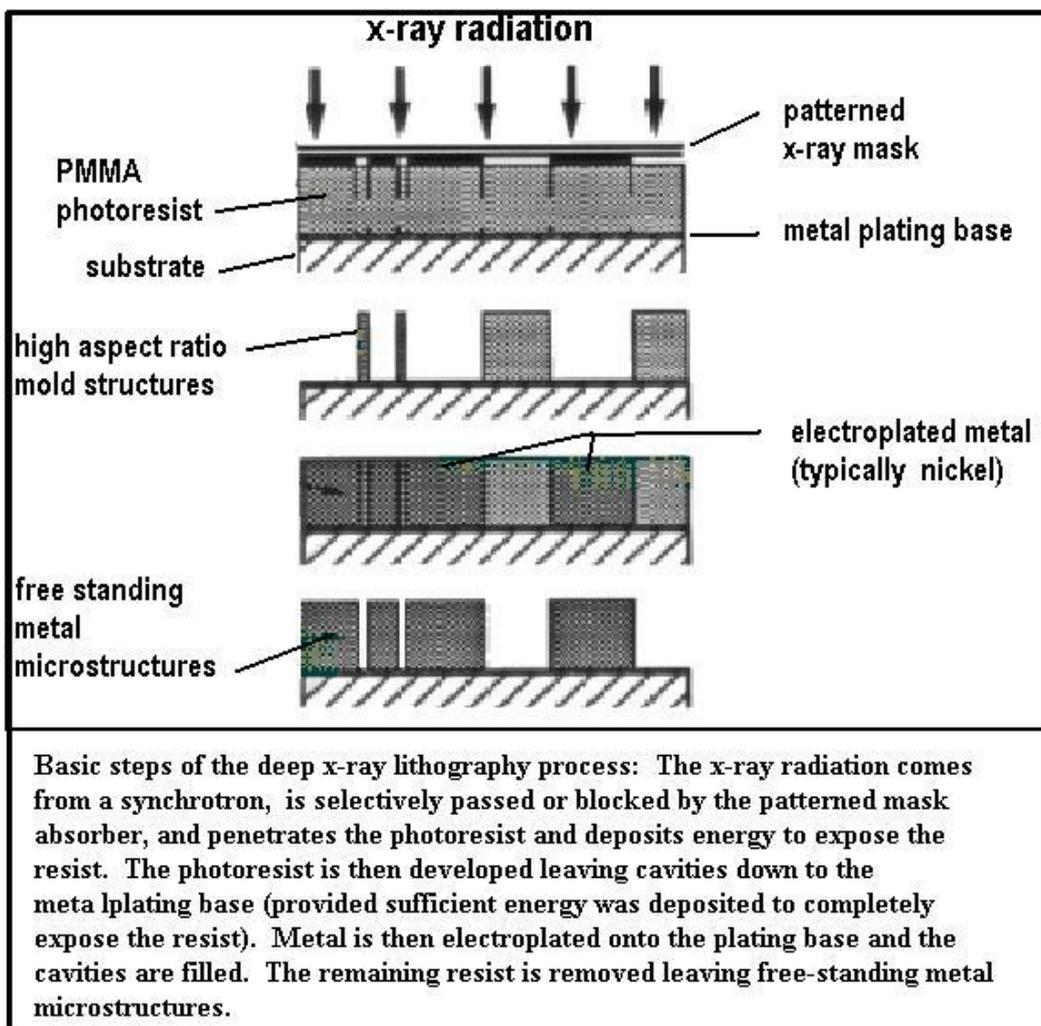
**Key EUV sub-systems**

EUV lithography tools typically utilize a plasma source to generate the 13.5 nm photons. EUV light from the plasma is gathered using an optical element called a ‘collector’. Light from the collector is directed into a set of shaping optics collectively known as the ‘illumination optics.’ This light illuminates a photomask located on a high scan-speed vacuum stage. The illumination optics consists of multilayer-coated normal incidence mirrors as well as grazing incidence mirrors. EUV masks consist of a six inch square, quarter inch thick low thermal expansion material with a multilayer reflective coating and an absorber layer, typically chrome, etched into the design of a circuit layer. The reflected image of the EUV mask enters a projection optic with a demagnification, typically 4:1. The projection optics are typically a collection of six or more multilayer mirrors and has an  $NA > 0.25$ . The final image is focused onto a silicon wafer coated with a photo-sensitive etch resist chemical emulsion or photoresist. The wafer is located on a high scan-speed vacuum-based stage. Each of these sub-systems, from plasma source to wafer stage, operates in a low-hydrocarbon, high vacuum environment.

### **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. 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 [LIGA is a German acronym for *Lithographie, Galvanoformung, Abformung* (Lithography, Electroplating, and Molding) that describes a fabrication technology used to create high-aspect-ratio microstructures.] 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.

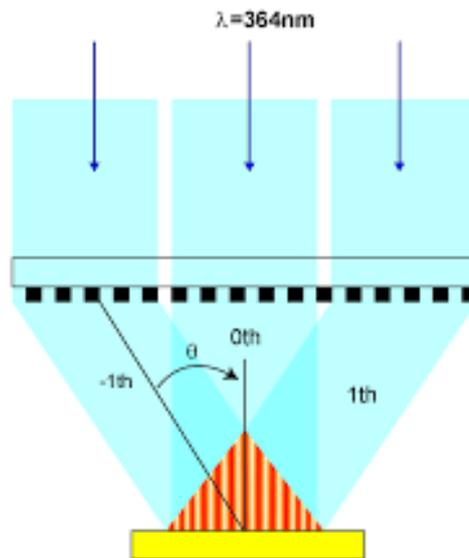


## Laser Interference Lithography

**Laser Interference lithography** is a technique for patterning regular arrays of fine features, without the use of complex optical systems or photomasks. The basic principle is the same as in interferometry or holography. An interference pattern between two or more coherent light waves is set up and recorded in a recording layer (photoresist). This interference pattern consists of a periodic series of fringes representing intensity minima and maxima. Upon post-exposure photolithographic processing, a photoresist pattern corresponding to the periodic intensity pattern emerges. For 2-beam interference, the fringe-to-fringe spacing or period is given by  $(\lambda/2)/\sin(\theta/2)$ , where  $\lambda$  is the wavelength and  $\theta$  is the angle between the two interfering waves. The minimum period achievable is then half the wavelength. By using 3-beam interference, arrays with hexagonal symmetry can be generated, while with 4 beams, arrays with rectangular symmetry are generated. Hence, by superimposing different beam combinations, different patterns are made possible.

For interference lithography to be successful, coherence requirements must be met. First, a spatially coherent light source must be used. This is effectively a point light source in combination with a collimating lens. A laser or synchrotron beam are also often used directly without additional collimation. The spatial coherence guarantees a uniform wavefront prior to beam splitting. Second, it is preferred to use a monochromatic or temporally coherent light source. This is readily achieved with a laser but broadband sources would require a filter. The monochromatic requirement can be lifted if a diffraction grating is used as a beam splitter, since different wavelengths would diffract into different angles but eventually recombine anyway. Even in this case, spatial coherence and normal incidence would still be required.

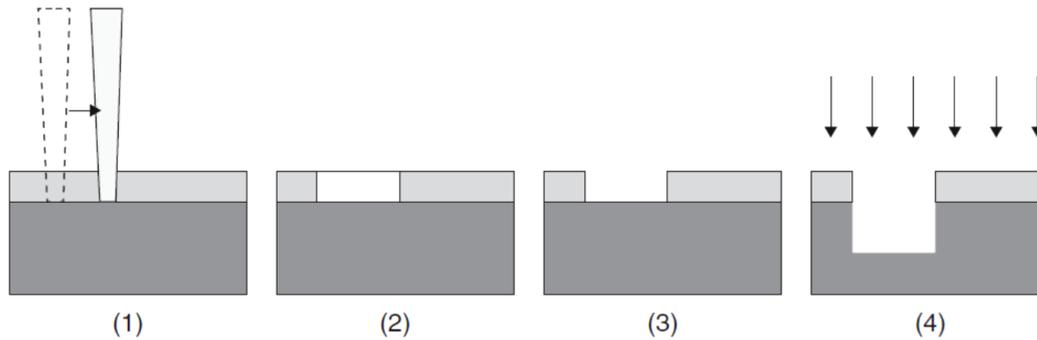
The benefit of using interference lithography is the quick generation of dense features over a wide area without loss of focus. Hence, it is commonly used for testing photoresist processes for lithography techniques based on new wavelengths (e.g., EUV or 193 nm immersion). In addition, interfering laser beams of high-power pulsed lasers provides the opportunity of applying a direct treatment of the material's surface (including metals, ceramics and polymers) based on photothermal and/or photochemical mechanisms. Due to the above mentioned characteristics, this method has been called in this case "Direct Laser Interference Patterning" (DLIP). Using DLIP, the substrates can be structured directly in one-step obtaining a periodic array on large areas in a few seconds. Such patterned surfaces can be use for different applications including tribology (wear and friction reduction) or biotechnology. Electron interference lithography may be used for patterns which normally take too long for conventional [[electron beam lithography](Pattern Matcher(lens))] to generate.



The drawback of interference lithography is that it is limited to patterning arrayed features only. Hence, for drawing arbitrarily shaped patterns, other photolithography techniques are required. In addition, non-optical effects, such as secondary electrons from ionizing radiation or photoacid generation and diffusion, cannot be avoided with interference lithography. For instance, the secondary electron range is roughly indicated by the width of carbon contamination ( $\sim 20\text{ nm}$ ) at the surface induced by a focused ( $2\text{ nm}$ ) electron beam. This indicates that the lithographic patterning of  $20\text{ nm}$  half-pitch features or smaller will be significantly affected by factors other than the interference pattern, such as the cleanliness of the vacuum.

### Electron beam lithography

Electron beam lithography, also known as e-beam lithography, is the process of tracing out a pattern in a suitable recording medium using a focused e-beam. The underlying physical mechanism relies on the fact that the recording medium, typically a thin organic polymer film, is altered by the passage of fast electrons. The recording medium is generally called *resist*. In a subsequent development step, the exposed material is removed (positive-tone process). Alternatively, the unexposed material is removed (negative-tone process). In either case, the result is a patterned film, which acts as a binary mask for further processing. This processing might include reactive ion etching, selective ion implantation, electroplating, or physical vapor deposition, to name a few. The patterned binary mask is a versatile and inexpensive enabler for a variety of subsequent processes. By superimposing multiple pattern layers, an enormous variety of useful devices can be fabricated. A typical positive-tone process is shown schematically in the following figure.



3.1 Typical positive-tone resist process. From left to right: electron beam scans (1) and leaves behind a latent image in the resist layer (2). Exposed resist (3) dissolves in the development process. Subsequent reactive ion etch (RIE) selectively removes substrate material (4), using the developed resist layer as a binary mask.

A focused e-beam represents the smallest, finest practical writing pencil known. The ultimate electron optical resolution is the same as an electron microscope, in the range of 0.06-0.15 nm, depending on the energy of the incident electrons. Ultimate lithographic resolution is not limited by the electron optics, but by the range of interaction of the beam electrons with the resist layer by scattering and secondary processes. Ultimate lithographic resolution is typically in the range of a few nanometers, depending on the energy of the electrons and the specific nature of the resist. This is about an order of magnitude smaller than the lithographic resolution obtainable with conventional optical lithography.

The pattern data are typically created using commercially available software for computer-aided design. These data must then be converted to a format usable by the e-beam writer. A digital electronic data path automatically converts and sends the data to the e-beam writer. The e-beam is then scanned over the writing surface using electric or magnetic fields, and turned on and off while it scans. Practically any arbitrary binary pattern can be written in this way.

In conventional optical lithography, one forms a demagnified image of a pre-existing patterned mask onto a resist-coated wafer. The mask can be used repeatedly to make many copies of the same pattern. In high-volume manufacturing of semiconductor chips, the patterns are highly complex. For example, 30 nm minimum-sized features might be distributed over a 30 mm square area. This represents an upper limit of 10-12 pattern features. Consequently, the mask can be expensive and time-consuming to fabricate. It is only cost-effective if many wafers are exposed with a single mask, since the cost of the mask is amortized over all of the wafers exposed.

E-beam lithography does not require a pre-existing mask, since the pattern is created and transmitted electronically. This permits great flexibility in trying out a large number of different patterns in a short time. This is ideal for low-volume applications, in which few copies of a given pattern are needed. An e-beam writer is a pattern *generator*, whereas a conventional optical lithography tool is a pattern

*replicator*. Incidentally, the method of choice for patterning masks for optical lithography is e-beam lithography.

An e-beam lithography system is comprised of several subsystems, including

- ❖ an electron optical column, to produce the focused e-beam;
- ❖ analog electronics to produce, focus, blank/unblank, and scan the beam;
- ❖ digital electronics to store and transmit the pattern data;
- ❖ a high-precision mechanical XY stage to position the writing substrate relative to the e-beam;
- ❖ a high-vacuum system, with provision to move the writing substrate in and out of the vacuum;
- ❖ high-speed computers and microprocessors, to automatically perform all of the necessary tasks;
- ❖ an extensive software system.

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.

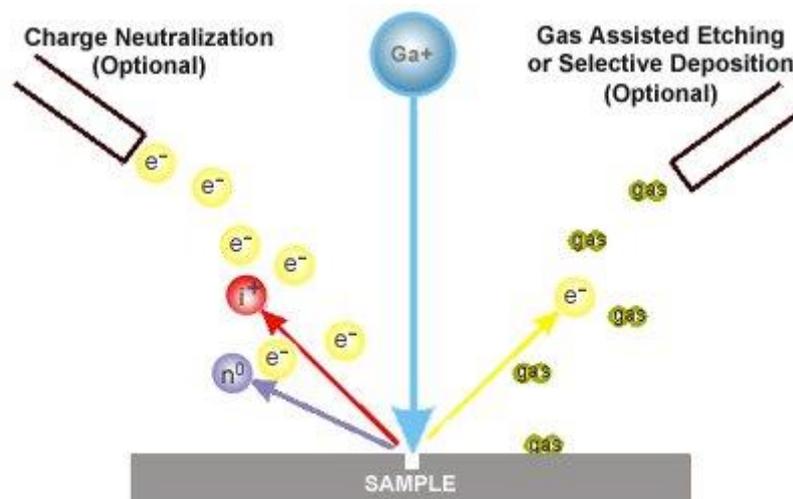
Physical defects are more varied, and can include sample charging (either negative or positive), backscattering calculation errors, dose errors, fogging (long-range reflection of backscattered electrons), contamination, beam drift and particles. Since the write time for electron beam lithography can 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.

### **Focused Ion Beam (FIB)**

FIBs produce tiny beams of a variety of positive ions (diameters from sub-nanometer to a few micrometers) energetic enough (from a few keV to ~ 150 keV) to cause the removal of sample material by elastic collisions (sputtering) at currents ranging from sub-pA to  $\mu\text{A}$ . This milling capability is localized on the sample at sizes from nanometers to microns and is at present the mainstay of work for FIBs. In addition to milling, ions can be selectively implanted into the sample. With the introduction of gases near the surface of the sample, material (either metals or insulators) can be deposited onto the sample at beam size dimensions to form novel structures. Due to the interaction of the ions with the

sample through inelastic collisions, secondary electrons and ions are emitted from the sample. The FIB can be used as a microscope yielding information different from that of a scanning electron microscope (SEM), and by collecting and separating the secondary ions produced by the beam, secondary-ion mass spectrometry (SIMS) can be performed at high spatial resolution.

FIB systems use a finely focused beam of ions (usually gallium) that can be operated at low beam currents for imaging or high beam currents for site specific sputtering or milling. As the diagram on the below shows, the gallium ( $\text{Ga}^+$ ) primary ion beam hits the sample surface and sputters a small amount of material, which leaves the surface as either secondary ions ( $i^+$  or  $i^-$ ) or neutral atoms ( $n^0$ ). The primary beam also produces secondary electrons ( $e^-$ ). As the primary beam raster's on the sample surface, the signal from the sputtered ions or secondary electrons is collected to form an image.

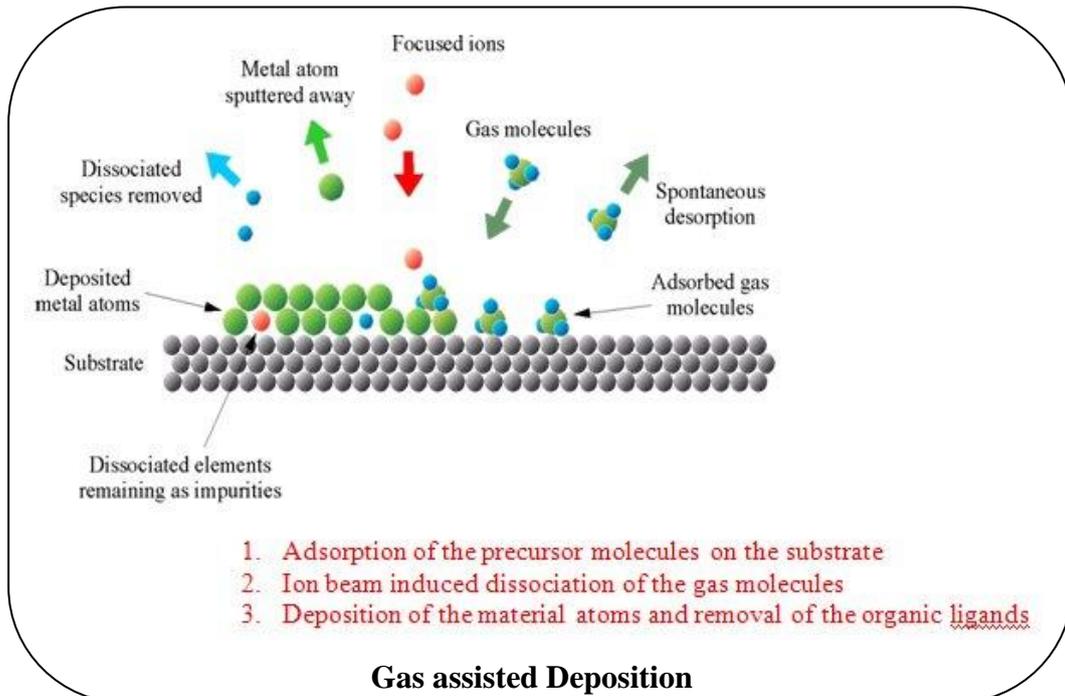


At low primary beam currents, very little material is sputtered and modern FIB systems can easily achieve 5 nm imaging resolution (imaging resolution with Ga ions is limited to  $\sim 5$  nm by sputtering and detector efficiency). At higher primary currents, a great deal of material can be removed by sputtering, allowing precision milling of the specimen down to a sub micrometer or even a nano scale. If the sample is non-conductive, a low energy electron flood gun can be used to provide charge neutralization. In this manner, by imaging with positive secondary ions using the positive primary ion beam, even highly insulating samples may be imaged and milled without a conducting surface coating, as would be required in an SEM.

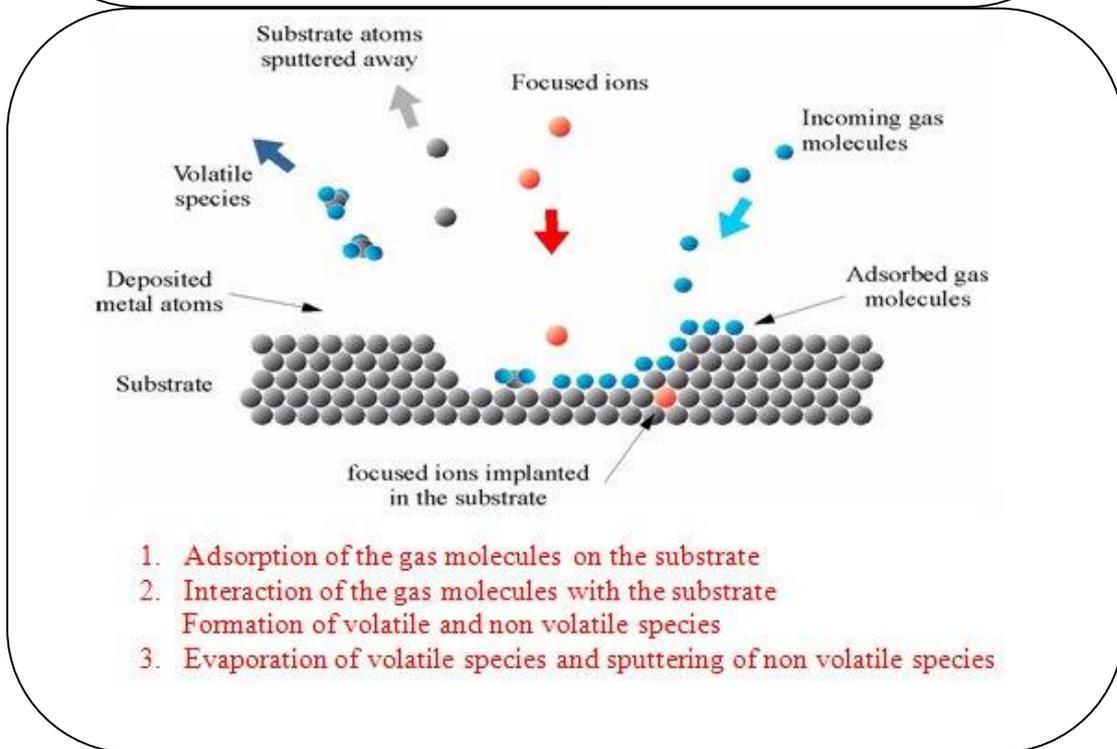
Most widespread instruments are using liquid-metal ion sources (LMIS), especially gallium ion sources. Ion sources based on elemental gold and iridium are also available. In a gallium LMIS, gallium metal is placed in contact with a tungsten needle and heated gallium wets the tungsten and flows to the

tip of the needle where the opposing forces of surface tension and electric field form the gallium into a cusp shaped tip called a Taylor cone. The tip radius of this cone is extremely small (~2 nm). The huge electric field at this small tip (greater than  $1 \times 10^8$  volts per centimeter) causes ionization and field emission of the gallium atoms. Source ions are then generally accelerated to an energy of 1–50 keV (kiloelectronvolts), and focused onto the sample by electrostatic lenses. LMIS produce high current density ion beams with very small energy spread. A modern FIB can deliver tens of nanoamperes of current to a sample, or can image the sample with a spot size on the order of a few nanometers. Unlike an electron microscope, FIB is inherently destructive to the specimen. When the high-energy gallium ions strike the sample, they will sputter atoms from the surface. Gallium atoms will also be implanted into the top few nanometers of the surface, and the surface will be made amorphous. Because of the sputtering capability, the FIB is used as a micro- and nano-machining tool, to modify or machine materials at the micro- and nanoscale. FIB micro machining has become a broad field of its own, but nano machining with FIB is a field that is still developing. Commonly the smallest beam size for imaging is 2.5–6 nm. The smallest milled features are somewhat larger (10–15 nm) as this is dependent on the total beam size and interactions with the sample being milled.

FIB tools are designed to etch or machine surfaces, an ideal FIB might machine away one atom layer without any disruption of the atoms in the next layer, or any residual disruptions above the surface. Yet currently because of the sputter the machining typically roughens surfaces at the submicrometre length scales. A FIB can also be used to deposit material via ion beam induced deposition. FIB-assisted chemical vapor deposition occurs when a gas, such as tungsten hexacarbonyl ( $W(CO)_6$ ) is introduced to the vacuum chamber and allowed to chemisorb onto the sample. By scanning an area with the beam, the precursor gas will be decomposed into volatile and non-volatile components; the non-volatile component, such as tungsten, remains on the surface as a deposition. This is useful, as the deposited metal can be used as a sacrificial layer, to protect the underlying sample from the destructive sputtering of the beam. From nanometers to hundred of micrometers in length, tungsten metal deposition allows metal lines to be put right where needed. Other materials such as platinum, cobalt, carbon, gold, etc., can also be locally deposited. Gas assisted deposition and FIB etching process are shown diagram.



### Gas assisted Deposition



### Gas assisted FIB etching

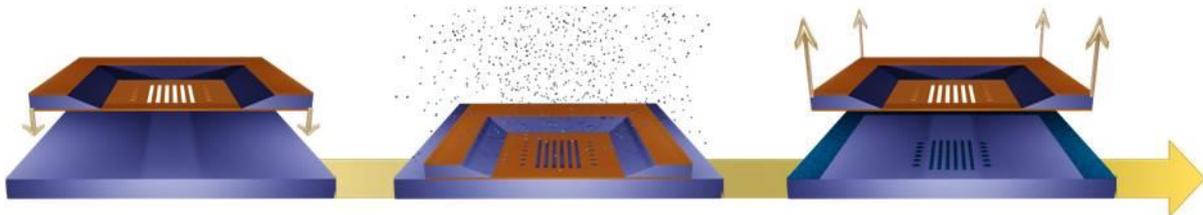
FIB is often used in the semiconductor industry to patch or modify an existing semiconductor device. For example, in an integrated circuit, the gallium beam could be used to cut unwanted electrical connections, and/or to deposit conductive material in order to make a connection. The high level of surface interaction is exploited in patterned doping of semiconductors. FIB is also used for maskless implantation. The drawbacks to FIB sample preparation are the above-mentioned surface damage and

implantation, which produce noticeable effects when using techniques such as high-resolution "lattice imaging" TEM or electron energy loss spectroscopy. This damaged layer can be minimised by FIB milling with lower beam voltages, or by further milling with a low-voltage argon ion beam after completion of the FIB process.

### **Shadow Mask evaporation lithography or stencil lithography**

Stencil lithography was first reported in a scientific journal as a micro-structuring technique by S. Gray and P. K. Weimer in 1959. They used long stretched metallic wires as shadow masks during metal deposition. Various materials can be used as membranes, such as metals, Si, Si<sub>x</sub>N<sub>y</sub>, and polymers. Today the stencil apertures can be scaled down to sub-micrometer size at full 4" wafer scale. This is called a nanostencil. Nano-scale stencil apertures have been fabricated using laser interference lithography (LIL), electron beam lithography, and focused ion beam lithography.

Stencil lithography is a novel method of fabricating nanometer scale patterns using nanostencils, stencils (shadow mask) with nanometer size apertures. It is a resist-less, simple, parallel nanolithography process, and it does not involve any heat or chemical treatment of the substrates (unlike resist-based techniques).



Several processes are available using stencil lithography: material deposition and etching, as well as implantation of ions. Different stencil requirements are necessary for the various processes, e. g. an extra etch-resistant layer on the backside of the stencil for etching (if the membrane material is sensitive to the etching process) or a conductive layer on the backside of the stencil for ion implantation.

The main deposition method used with stencil lithography is physical vapor deposition. This includes thermal and electron beam physical vapor deposition, molecular beam epitaxy, sputtering, and pulsed laser deposition. The more directional the material flux is, the more accurate the pattern is transferred from the stencil to the substrate.

There are three main modes of operation of stencil lithography: static, quasi-dynamic and dynamic. While all the above described processes have been proven using the static mode (stencil doesn't move relative to substrate during material or ion processing), only ion implantation has been shown for the non-static modes (quasi-dynamic).

#### **Static mode**

In the static mode, the stencil is aligned (if necessary) and fixed to a substrate. The stencil-substrate pair is placed in the evaporation/etching/ion implantation machine, and after the processing is done, the stencil is simply removed from the now patterned substrate.

### **Quasi static**

In the quasi-dynamic mode (or step-and-repeat), the stencil moves relative to the substrate in between depositions, without breaking the vacuum.

### **Dynamic stencil**

In the dynamic mode, the stencil moves relative to the substrate during deposition, allowing the fabrication of patterns with variable height profiles by changing the stencil speed during a constant material deposition rate.

Despite it being a versatile technique, there are still several challenges to be addressed by stencil lithography. During deposition through the stencil, material is deposited not only on the substrate through the apertures but also on the stencil backside, including around and inside the apertures. This reduces the effective aperture size by an amount proportional to the deposited material, leading ultimately to aperture **clogging**. The accuracy of the pattern transfer from the stencil to the substrate depends on many parameters. The material diffusion on the substrate (as a function of temperature, material type, evaporation angle) and the geometrical setup of the evaporation are the main factors. Both lead to an enlargement of the initial pattern, called **blurring**.

### **Probe lithography or scanning probe lithography**

**Scanning probe lithography** (SPL) describes a set of nanolithographic methods to pattern material on the nanoscale using scanning probes. It is a direct-write, mask-less approach which bypasses the diffraction limit and can reach resolutions below 10 nm. It is considered an alternative lithographic technology often used in academic and research environments. The term *scanning probe lithography* was coined after the first patterning experiments with scanning probe microscopes (SPM) in the late 1980s. There are different classes of probe lithography's. They are classified according to their goal to either add or remove material, by the general nature of the process either chemical or physical, or according to the driving mechanisms of the probe-surface interaction used in the patterning process: mechanical, thermal, diffusive and electrical.

### **Mechanical/thermo-mechanical**

**Mechanical scanning probe lithography** (m-SPL) is a nanomachining or *nano-scratching* top-down approach without the application of heat. Thermo-mechanical SPL applies heat together with a mechanical force, e.g. indenting of polymers in the Millipede memory.

**Thermal:** **Thermal scanning probe lithography** (t-SPL) uses a heatable scanning probe in order to efficiently remove material from a surface without the application of significant mechanical forces. The patterning depth can be controlled to create high-resolution 3D structures

**Thermo-chemical:** Thermochemical scanning probe lithography (tc-SPL) or *thermochemical nanolithography* (TCNL) employs the scanning probe tips to induce thermally activated chemical reactions to change the chemical functionality or the phase of surfaces. Such thermally activated reactions have been shown in proteins, organic semiconductors, electroluminescent conjugated polymers, and nanoribbonresistors. Furthermore, deprotection of functional groups (sometimes involving a temperature gradients), reduction of oxides, and the crystallization of piezoelectric/ferroelectric ceramics has been demonstrated.

#### **Dip pen/ Thermal dip-pen**

Dip-pen scanning probe lithography (dp-SPL) or *dip-pen nanolithography* (DPN) is a scanning probe lithography technique based on diffusion, where the tip is employed to create patterns on a range of substances by deposition of a variety of liquid inks. Thermal dip-pen scanning probe lithography or *thermal dip-pen nanolithography* (TDPN) extends the usable inks to solids, which can be deposited in their liquid form when the probes are pre-heated.

#### **Bias induced**

Bias-induced scanning probe lithography (b-SPL) uses the high electrical fields created at the apex of a probe tip when voltages are applied between tip and sample to facilitate and confining a variety of chemical reactions to decompose gases or liquids in order to locally deposit and grow materials on surfaces.

Being a serial technology, SPL is inherently slower than e.g. photolithography or nanoimprint lithography, while parallelization as required for mass-fabrication is considered a large systems engineering effort. As for resolution, SPL methods bypass the optical diffraction limit due to their use of scanning probes compared with photolithographic methods. Some probes have integrated in-situ metrology capabilities, allowing for feedback control during the write process. SPL works under ambient atmospheric conditions, without the need for ultra high vacuum (UHV), unlike e-beam or EUV lithography.

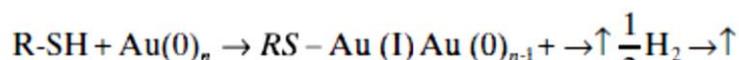
## Nano Imprint Lithography

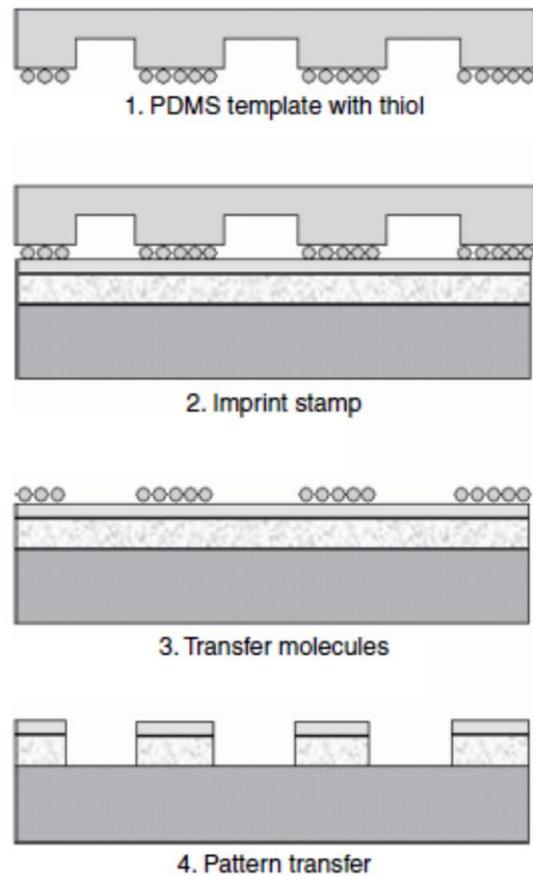
Imprint lithography is essentially a micromolding process in which the topography of a template defines the patterns created on a substrate. When the printing is done at the nanoscale the various imprint methods are generally referred to as NIL. Investigations by several researchers indicate that imprint lithography resolution is limited only by the resolution of the template fabrication process. The most famous example of this capability is the reproduction of a 2 nm carbon nanotube by the John Rogers Research group at the University of Illinois. NIL possesses other important advantages over conventional photolithography, since it does not require expensive projection optics, advanced illumination sources, or specialized resist materials that are central to the operation of these technologies. There are three basic approaches to imprint lithography: soft lithography (SL), thermal nanoimprint lithography (T-NIL), and UV-NIL.

### Soft Lithography

SL, also known as microcontact printing ( $\mu$ CP), generally refers to the process of transferring a self-assembled monolayer using a flexible template. The invention of the technology dates back to 1994, and is the result of work from the laboratory of George Whitesides at Harvard. The technology surfaced mainly as a quick and easy way for students to print small geometries in a laboratory environment. Whitesides *et al.* formed a template by applying a liquid precursor to polydimethylsiloxane (PDMS) over a master mask produced using either electron beam or optical lithography. The liquid is cured, and the PDMS solid is peeled away from the original mask. The PDMS is essentially an elastomeric material, consisting of a polymer chain of silicon containing oils. Typical mechanical properties include a tensile strength of 7.1 MPa, an elongation at break of 140%, and tear strength of 2.6 kN/m. As a result, relative to either silicon or fused silica, it is quite workable.

Once prepared, the PDMS template can then be coated with a thiol ink solution, such as an alkanethiol. The imprint process is depicted in Figure in the next page. The thiol molecules are subsequently transferred to a substrate, coated with a thin layer of gold, thereby forming a self-assembled monolayer (SAM) on the gold surface. The nature of the gold-sulfur bond is still not completely understood. R. S. Kane *et al.* postulate that the species present at the surface of the gold is a gold thiolate





Process schematic for nano imprint lithography

To prevent adhesion between the master and daughter masks, the master surface is passivated by the gas phase deposition of a long-chain, fluorinated alkylchlorosilane ( $\text{CF}_3(\text{CF}_2)_6(\text{CH}_2)_2\text{SiCl}_3$ ). The fluorosilane reacts with the free silanol groups on the surface of the master to form a Teflon-like surface with a low interfacial free energy. The passivated surface acts as a release layer that facilitates the removal of the PDMS stamp from the master.

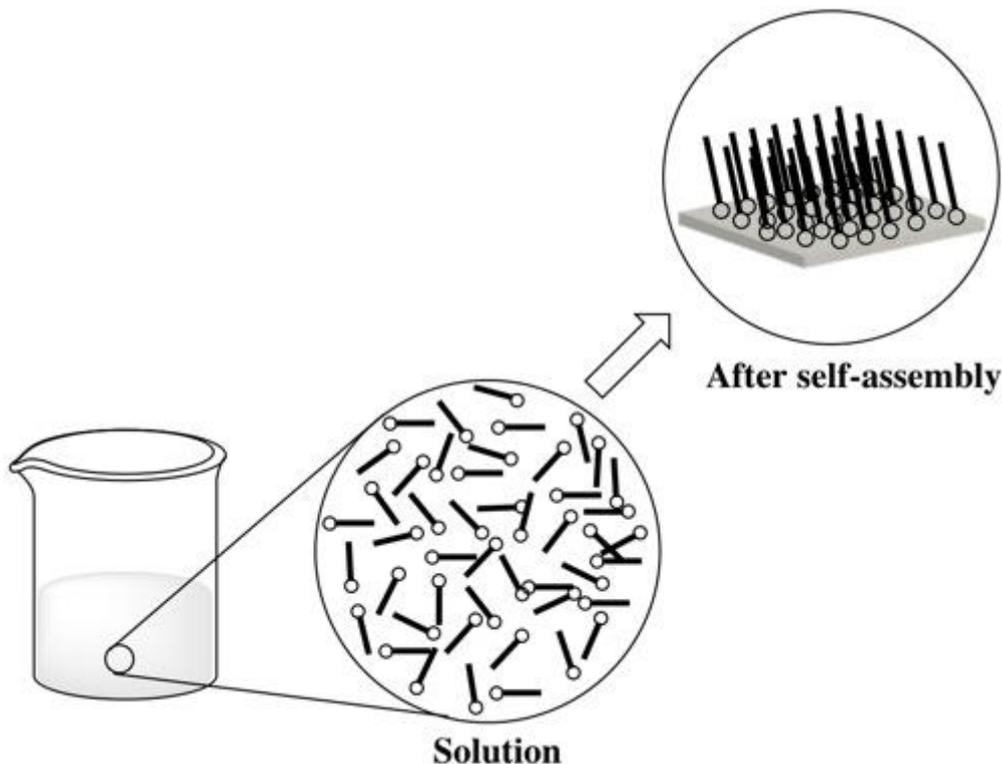
The pattern transfer process starts with a wet etch of the thin gold film. A wet etch is typically used, since gold is not readily reactively ion etched. Although it is possible to sputter etch gold, the thin thiol layer would not hold up to such a process. The gold film then acts as an etch mask for any underlying materials. Because gold is a soft metal, it is often necessary to include a second hard mask beneath the gold.

The range of feature sizes that can be imprinted with this technology is quite broad. While squares and lines with geometries of several microns are easily achieved, smaller circular features with dimensions as small as 30 nm have also been demonstrated.

## Self Assembly of Nano particles

**Self-assembly** is a phenomenon where the components of a system assemble themselves spontaneously via an interaction to form a larger functional unit. This spontaneous organization can be due to direct specific interaction and/or indirectly through their environment. Due to the increasing technological advancements, the study of materials in the nanometre scale is becoming more important. The ability to assemble nanoparticles into well-defined configuration in space is crucial to the development of electronic devices that are small but can contain plenty of information. The spatial arrangements of these self-assembled nanoparticles can be potentially used to build increasingly complex structures leading to a wide variety of materials that can be used for different purposes.

At the molecular level, intermolecular force hold the spontaneous gathering of molecules into a well-defined and stable structure together. In chemical solutions, self-assembly is an outcome of random motion of molecules and the affinity of their binding sites for one another. In the area of nanotechnology, developing a simple, efficient method to organize molecules and molecular clusters into precise, pre-determined structure is crucial.



An example of self-assembly of nanoparticles in a solution. In this diagram, it can be seen that a disordered system formed an organized structure which can be due to specific interactions among the particles.

## **Particle Interaction**

Intermolecular forces govern the particle interaction in self-assembled systems. The forces tend to be intermolecular in type rather than ionic or covalent because ionic or covalent bonds will “lock” the assembly into non-equilibrium structures. The types intermolecular forces seen in self-assembly processes are van der Waals, hydrogen bonds, and weak polar forces, just to name a few. In self-assembly, regular structural arrangements are frequently observed, therefore there must be a balance of attractive and repulsive between molecules otherwise an equilibrium distance will not exist between the particles. The repulsive forces can be electron cloud-electron cloud overlap or electrostatic repulsion.

Typically, nanoparticles will self-assemble for one or both of two reasons: molecular interactions and external direction. Recently, researchers are more interested in the latter of these two reasons, and are able to apply external directing to a large variety of systems.

## **Self Assembly by Molecular Interactions**

Nanoparticles have the ability to assemble chemically through covalent or noncovalent interactions with their capping ligand. The terminal functional group(s) on the particle are known as capping ligands. As these ligands tend to be complex and sophisticated, self-assembly can provide a simpler pathway for nanoparticle organization by synthesizing efficient functional groups.

## **Intermolecular Forces**

Nanoparticles can self-assemble as a result of their intermolecular forces. As systems look to minimize their free energy, self-assembly is one option for the system to achieve its lowest free energy thermodynamically. Nanoparticles can be programmed to self-assemble by changing the functionality of their side groups, taking advantage of weak and specific intermolecular forces to spontaneously order the particles. These direct interparticle interactions can be typical intermolecular forces such as hydrogen bonding or Van der Waals forces, but can also be internal characteristics, such as hydrophobicity or hydrophilicity. For example, lipophilic nanoparticles have the tendency to self-assemble and form crystals as solvents are evaporated. While these aggregations are based on intermolecular forces, external factors such as temperature and pH also play a role in spontaneous self-assembly.

## **Hamaker Interaction**

As nanoparticle interactions take place on a nanoscale, the particle interactions must be scaled similarly. Hamaker interactions take into account the polarization characteristics of a large number of nearby particles and the effects they have on each other. Hamaker interactions sum all of the forces between all particles and the solvent(s) involved in the system. While Hamaker theory generally describes a

macroscopic system, the vast number of nanoparticles in a self assembling system allows the term to be applicable. Hamaker constants for nanoparticles are calculated using Lifshitz theory, and can often be found in literature.

### **Directed Self Assembly**

The natural ability of nanoparticles to self-assemble can be replicated in systems that do not intrinsically self-assemble. Directed self-assembly (DSA) attempts to mimic the chemical properties of self-assembling systems, while simultaneously controlling the thermodynamic system to maximize self-assembly.

### **Electric and Magnetic Fields**

External fields are the most common directors of self-assembly. Electric and magnetic fields allow induced interactions to align the particles. The fields take advantage of the polarizability of the nanoparticle and its functional groups. When these field-induced interactions overcome random Brownian motion, particles join to form chains and then assemble. At more modest field strengths, ordered crystal structures are established due to the induced dipole interactions. Electric and magnetic field direction requires a constant balance between thermal energy and interaction energies.

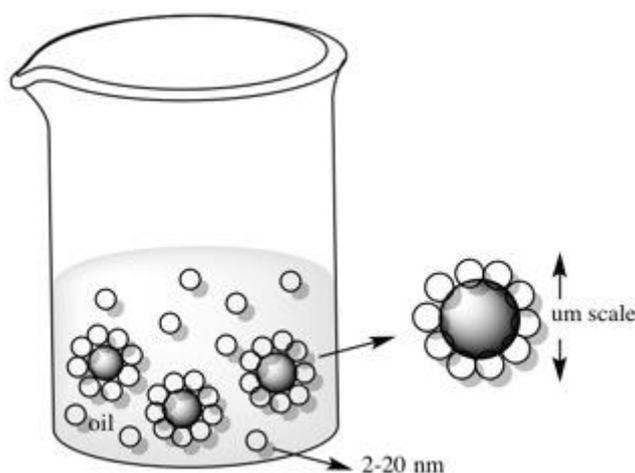
### **Solid Interfaces**

Nano-particles can self-assemble on solid surfaces after applying external forces (like magnetic, electric, and flow) as mentioned in the above section. Templates made of microstructures like carbon nanotubes or block polymers can also be used to assist in self-assembly; they cause directed self-assembly (DSA) in which active sites are embedded to selectively induce nanoparticle deposition. Such templates are considered as any object onto which different particles can be arranged into a structure with a morphology similar to that of the template. Carbon nanotubes (microstructures), single molecules, or block copolymers are common templates. Nanoparticles are often shown to self-assemble within distances of nanometers and micrometers, but block copolymer templates can be used to form well-defined self-assemblies over macroscopic distances. By incorporating active sites to the surfaces of nanotubes and polymers, the functionalization of these templates can be transformed to favor self-assembly of specified nanoparticles.

### **Liquid Interfaces**

Pickering and Ramsden explained the idea of pickering emulsions when experimenting with paraffin-water emulsions with solid particles like iron oxide and silicon dioxide. They observed that the micron-sized colloids generated a resistant film at the interface between the two immiscible phases, inhibiting the coalescence of the emulsion drops. These Pickering emulsions, as shown in the figure below, are

formed from the self-assembly of colloidal particles in two-part liquid systems, such as oil-water systems. The desorption energy, which is directly related to the stability of emulsions depends on the particle size, particle-particle interaction and, of course, particle-water and particle-oil interactions



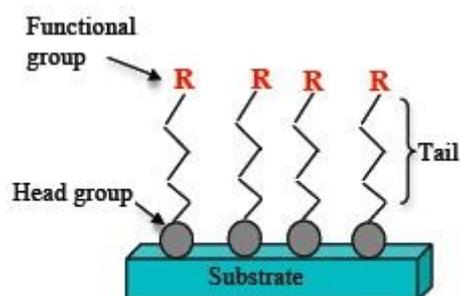
### Self assembled monolayers

**Self-assembled monolayers (SAM)** of organic molecules are molecular assemblies formed spontaneously on surfaces by adsorption and are organized into more or less large ordered domains. In some cases molecules that form the monolayer do not interact strongly with the substrate. This is the case for instance of the two-dimensional supramolecular networks of e.g. Perylene-tetracarboxylicacid-dianhydride (PTCDA) on gold or of e.g. porphyrins on highly oriented pyrolytic graphite (HOPG). In other cases the molecules possess a head group that has a strong affinity to the substrate and anchors the molecule to it. Such a SAM consisting of a head group, tail and functional end group is depicted in Figure 1. Common head groups include thiols, silanes, phosphonates, etc.

SAMs are created by the chemisorption of "head groups" onto a substrate from either the vapor or liquid phase followed by a slow organization of "tail groups". Initially, at small molecular density on the surface, adsorbate molecules form either a disordered mass of molecules or form an ordered two-dimensional "lying down phase", and at higher molecular coverage, over a period of minutes to hours, begin to form three-dimensional crystalline or semicrystalline structures on the substrate surface. The "head groups" assemble together on the substrate, while the tail groups assemble far from the substrate. Areas of close-packed molecules nucleate and grow until the surface of the substrate is covered in a single monolayer.

Adsorbate molecules adsorb readily because they lower the surface free-energy of the substrate and are stable due to the strong chemisorption of the "head groups." These bonds create monolayers that are more stable than the physisorbed bonds of Langmuir-Blodgett films. A Trichlorosilane based "head group", for example in a FDTS (Perfluorodecyltrichlorosilane) molecule reacts with an hydroxyl group

on a substrate, and forms very stable, covalent bond [R-Si-O-substrate] with an energy of 452 kJ/mol. Thiol-metal bonds, that are on the order of 100 kJ/mol, making the bond a fairly stable in a variety of temperature, solvents, and potentials. The monolayer packs tightly due to van der Waals interactions, thereby reducing its own free energy. The adsorption can be described by the Langmuir adsorption isotherm if lateral interactions are neglected.



### Layer by Layer assembly

**Layer-by-layer** (LbL) deposition is a thin film fabrication technique. The films are formed by depositing alternating layers of oppositely charged materials with wash steps in between. This can be accomplished by using various techniques such as immersion, spin, spray, electromagnetism, or fluidics

A simple representation can be made by defining two oppositely charged polyions as + and -, and defining the wash step as W. To make an LbL film with 5 bilayers one would deposit W+W-W+W-W+W-W+W-W+W-W+W-W, which would lead to a film with 5 bilayers, specifically + - + - + - + - .

It is important to note that the representation of the LbL technique as a multilayer build-up based solely on electrostatic attraction is a simplification. Other interactions are involved in this process, including hydrophobic attraction. Multilayer build-up is enabled by multiple attractive forces acting cooperatively, typical for high-molecular weight building blocks, while electrostatic repulsion provides self-limitation of the absorption of individual layers. This range of interactions makes it possible to extend the LbL technique to hydrogen-bonded films, nanoparticles, similarly charged polymers, hydrophobic solvents, and other unusual systems.

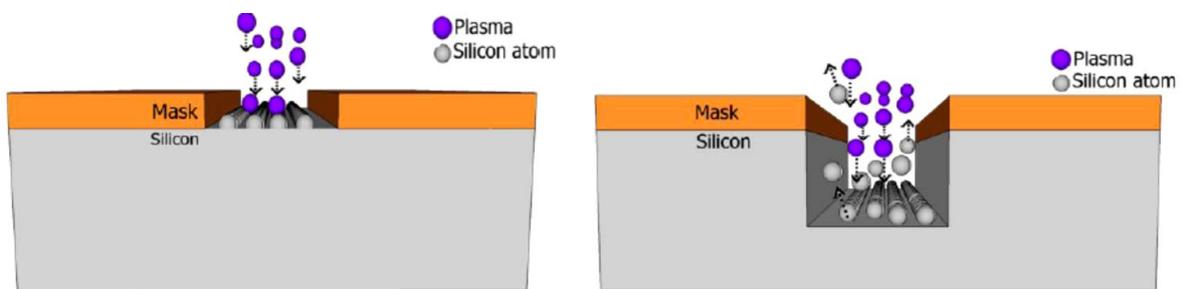
LbL offers several advantages over other thin film deposition methods. LbL is simple and can be inexpensive. There are a wide variety of materials that can be deposited by LbL including polyions, metals, ceramics, nanoparticles, and biological molecules. Another important quality of LbL is the high degree of control over thickness, which arises due to the variable growth profile of the films, which directly correlates to the materials used, the number of bilayers, and the assembly technique

## Dry etching

In dry etching, plasmas or etchant gasses remove the substrate material. The reaction that takes place can be done utilizing high kinetic energy of particle beams, chemical reaction or a combination of both.

### Physical dry etching:

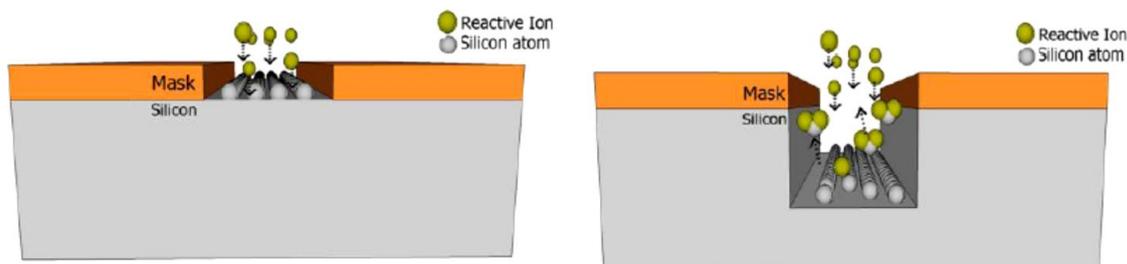
Physical dry etching requires high energy kinetic energy (ion, electron, or photon) beams to etch off the substrate atoms. When the high energy particles knock out the atoms from the substrate surface, the material evaporates after leaving the substrate. There is no chemical reaction taking place and therefore only the material that is unmasked will be removed. The physical reaction taking place is illustrated in Figure.



The plasma hits the silicon wafer with high energy to knock-off the Si atoms on the surface. (a) The plasma atoms hitting the surface. (b) The silicon atoms being evaporated off from the surface.

### Chemical dry etching:

Chemical dry etching (also called vapor phase etching) does not use liquid chemicals or etchants. This process involves a chemical reaction between etchant gases to attack the silicon surface. The chemical dry etching process is usually isotropic and exhibits high selectivity. Figure below shows a rendition of the reaction that takes place in chemical dry etching. Some of the ions that are used in chemical dry etching is tetrafluoromethane ( $\text{CF}_4$ ), sulfur hexafluoride ( $\text{SF}_6$ ), nitrogen trifluoride ( $\text{NF}_3$ ), chlorine gas ( $\text{Cl}_2$ ), or fluorine ( $\text{F}_2$ ).

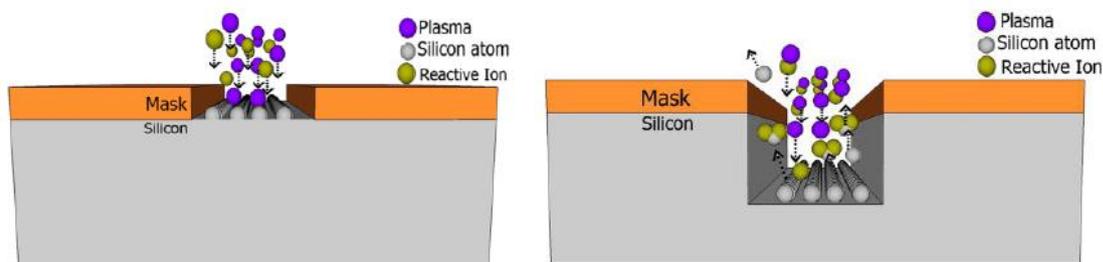


Process of a reactive ion interacting with the silicon surface. (a) The interaction between the reactive ion and the silicon atom. (b) A bond between the reactive ion and the silicon atom then chemically remove the silicon atoms from the surface.

Dry etching covers a family of methods by which a solid surface is etched in the gas or vapor phase, physically by ion bombardment, chemically by a chemical reaction through a reactive species at the surface, or by combined physical and chemical mechanisms. In semiconductor manufacturing plasma ashing is the process of removing the photoresist from an etched wafer. Using a plasma source, a monatomic reactive species is generated. Oxygen or fluorine are the most common reactive species. The reactive species combines with the photoresist to form ash which is removed with a vacuum pump.

### Reactive Ion Etching:

Reactive ion etching (RIE) uses both physical and chemical mechanisms to achieve high levels of resolution. The process is one of the most diverse and most widely used processes in industry and research. Since the process combines both physical and chemical interactions, the process is much faster. The high energy collision from the ionization helps to dissociate the etchant molecules into more reactive species.



This process involves both physical and chemical reactions to etch off the silicon. In the RIE-process, cations are produced from reactive gases which are accelerated with high energy to the substrate and chemically react with the silicon. The typical RIE gasses for Si are  $CF_4$ ,  $SF_6$  and  $BCl_2 + Cl_2$ .

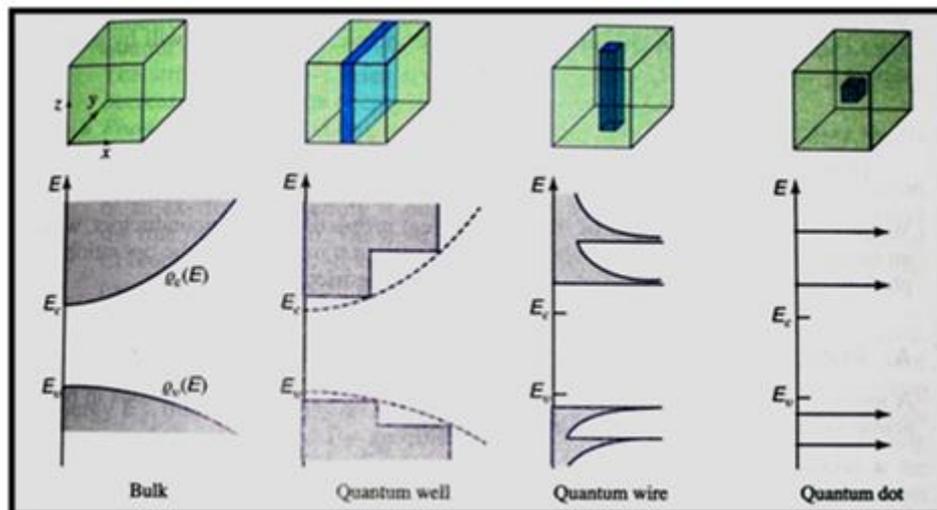
### Wet etching

Wet etching is a material removal process that uses liquid chemicals or etchants to remove materials from a wafer. The specific patterns are defined by masks on the wafer. Materials that are not protected by the masks are etched away by liquid chemicals. These masks are deposited and patterned on the wafers in a prior fabrication step using lithography. A wet etching process involves multiple chemical reactions that consume the original reactants and produce new reactants. The wet etch process can be described by three basic steps.

- (1) Diffusion of the liquid etchant to the structure that is to be removed.
- (2) The reaction between the liquid etchant and the material being etched away. A reduction-oxidation (redox) reaction usually occurs. This reaction entails the oxidation of the material then dissolving the oxidized material.
- (3) Diffusion of the byproducts in the reaction from the reacted surface.

### Quantum dots

- Quantum dots are semiconductors whose excitons are confined in all three dimensions of space.
- Quantum dots have properties combined between
  - Those of bulk semiconductors
  - Those of atoms
- Different methods to create quantum dots.
- Multiple applications.
- Electrons and holes are confined in all three dimensions of space by a surrounding material with a larger bandgap.
- Discrete energy levels (artificial atom).
- A quantum dot has a larger bandgap.
- Like bulk semiconductor, electrons tend to make transitions near the edges of the bandgap in quantum dots.

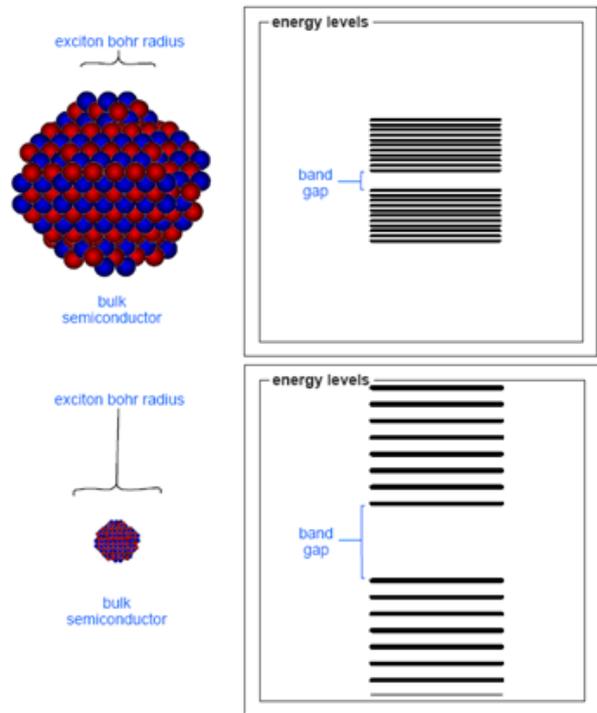


- Very small semiconductor particles with a size comparable to the Bohr radius of the excitons (separation of electron and hole).
  - Typical dimensions: 1 – 10 nm
  - Can be as large as several  $\mu\text{m}$ .
  - Different shapes (cubes, spheres, pyramids, etc.)

## Discrete Energy Levels

The energy levels depend on the size, and also the shape, of the quantum dot.

Smaller quantum dot: Higher energy required to confine excitons to a smaller volume. Energy levels increase in energy and spread out more. Higher band gap energy.



## How to Make Quantum Dots

There are three main ways to confine excitons in semiconductors:

Lithography

Colloidal synthesis

Epitaxy:

Patterned Growth

Self-Organized Growth