

CH62052: Instability Spring 2022-23 Department of Chemical Engineering Indian Institute of Technology Kharagpur

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Lab web page: https://sites.google.com/site/rmresearchgroup/home

Examples of Pattern in Nature

There are many objects and entities around us in nature which exhibit patterns







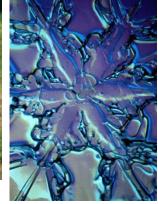






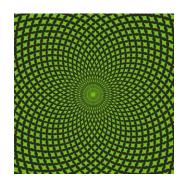


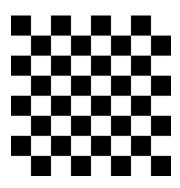






Man made patterns – Man as Patterens Patterns















Patterns at the Meso and nano scale

1 nm = 10⁻⁹ m Meso Scale: few to hundreds of nm

Here essentially we talk about how the patterns present on the surface of an object can lead to "exotic" properties.

These unique properties are NOT related to the chemical structure of the material, but results due to the presence of meso / nano scale surface features on the object.

Many extraordinary properties observed in nature are also attributed to presence of such patterns

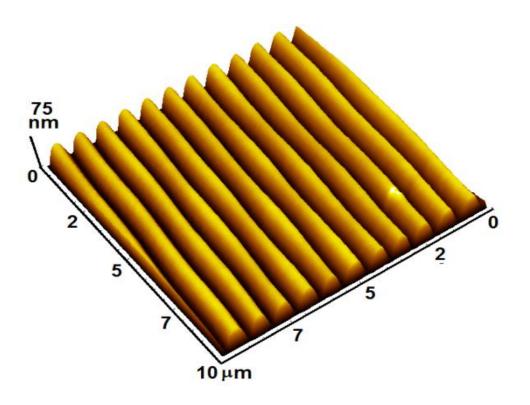
In addition, it may be possible to achieve extraordinary properties which are never found in nature by artificially patterning a surface (example can be negative Refractive Index Meta materials)

Patterns at the Meso and nano scale

Patterns can be Topographic Patterns

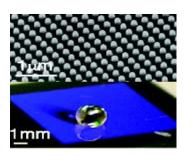
Or

Can be Chemical Patterns

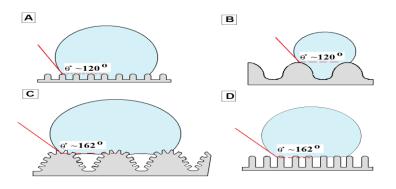


AFM Image (Atomic Force Microscope)

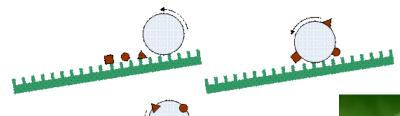
Application of Patterns: Structural Super Hydrophobicity







Self Cleaning Surfaces









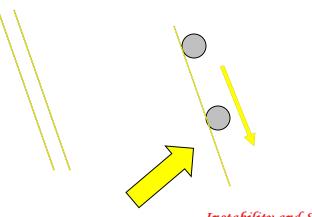
From the August 2008 Scientific American Magazine | 2 comments

Self-Cleaning Materials: Lotus Leaf-Inspired Nanotechnology

The lotus plant's magnificent ability to repel dirt has inspired a range of selfcleaning and antibacterial technologies that may also help control microfluidic "lab-on-a-chip" devices

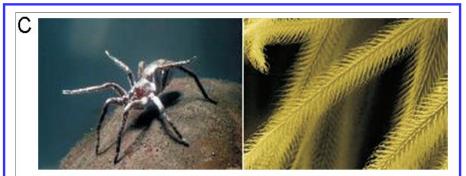
By Peter Forbes

Condensation



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Application of Patterned Surfaces

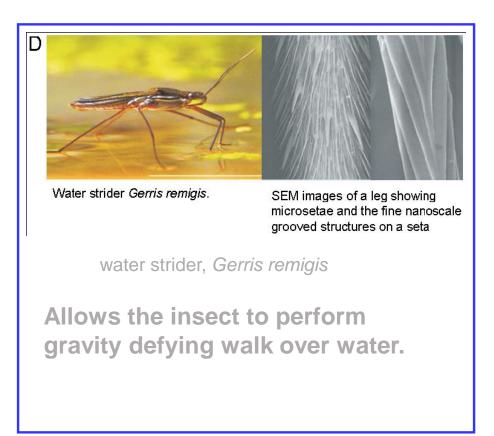


A silvery shining air layer encloses the fishing spider (*Ancylometes bogotensis*, left). Hairs of the fishing spider (right)

fishing spider Ancylometes bogotensis

Hairy structure is plastron

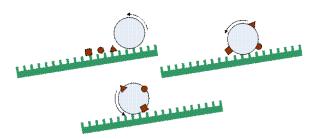
that allows the insect to breathe normally under submerged conditions



Simpler examples: Bird Feathers, most plant leaves

From V M NAIK, R MUKHERJEE, A MAJUMDER and A SHARMA, current trends in Science, Platinum Jubilee Special Issue of Indian Academy of Sciences, 2009 Page 129, available online

Self Cleaning Surfaces



The presence of the patterns hinders the adhesion of any dust particle to the surface.

Simultaneously it also exhibits super hydrophobicity so water drop nearly rolls off the surface

While rolling down, the drop pics up the dust on the surface.

Self Cleaning Coatings on a Solar Cell is a Major Area of Research These days!



Glass Facade in High Rise Buildings

Self Cleaning Surfaces

Application in Solar Cell Covers



Structural Color

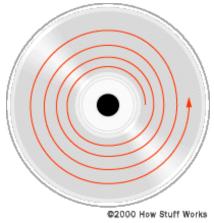


If you hold the back side of a CD or a DVD, then you see rainbow

The gap between adjacent turns of the spiral is 1.5 microns, which are being separated by a valley 750 nm wide

When visible light falls on such a surface

Diffraction of light occurs, resulting in the



Diffraction refers to various phenomena which occur when a wave encounters an obstacle and its effects are generally mo

Rainbow color

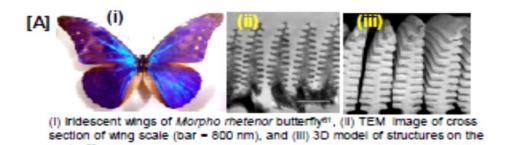
obstacle and its effects are generally most pronounced for waves where the wavelength is roughly similar to the dimensions of the diffracting objects

Wave Length of Visible Light: 400 – 700 nm

Chameleon (variety of slow lizard). Do they (or can they) Change Color!)



Structural Color



The color of many insects, including the brilliant color of a butterfly is STRUCTURAL in nature

The color does not originate from Pigments, but from Optical Diffraction due to the presence of sub micron surface structures.



Structural color allows insects (even many other category of creatures) to Camouflage on demand, as the color visible to the predator is a function of the illuminating light as well.

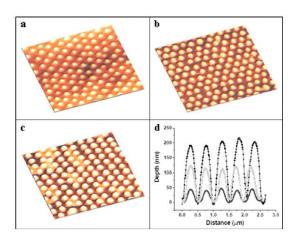
In many cases the color is a combined effect of pigmenting and diffraction

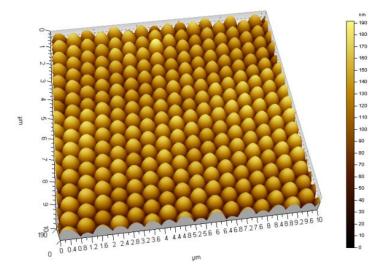
Other Optical Applications

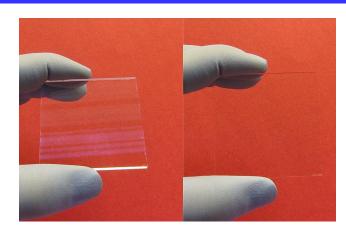
Holograms

Moth eye Effect (based on the concept of randomly structured graded index surfaces: for Anti Reflection Coating)

Optical Waveguides (Confines the propagation of light inside a medium)







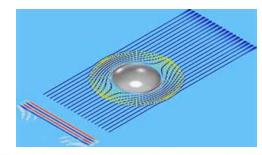




Meta Materials

Invisibility might be possible soon

Which are also known as negative Refractive Index Materials

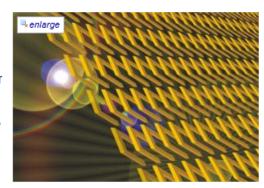






Towards Cloaking Visible Light: Three-dimensional Metamaterials For The Optical Wavelength Range

ScienceDaily (Dec. 24, 2007) — Last year researchers from Duke University stunned the world when they announced a cloaking device for the microwave range. This device made use of metamaterials that had a negative refractive index for electromagnetic radiation. The metamaterials were carefully designed split-ring resonators with a structure size much smaller than the wavelength. Only 10 stacked layers of metamaterials were necessary to achieve the desired invisibility effect.





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The BIGGEST application area of Patterning





Pentium II processor

200 M Hz Clock Speed

500 MBHDD

1999

To what is this change attributed to?



Intel Core i9-9980XE

4.5 GHz speed

5 TB HDD

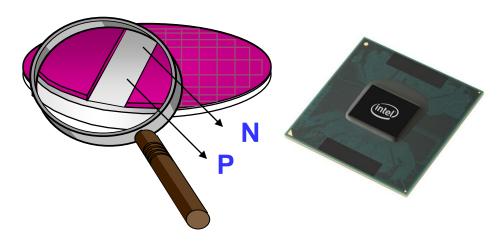
2019

Patterning in Micro Electronics

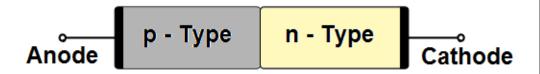
The micro electronic industry PC, Laptop, Cell Phone, i-pod

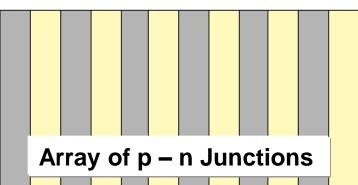
Have you ever thought how every year the speed of the computer processor becomes faster or how the memory sizes increases?

Reality is the tremendous progress in the field of micro electronics industry is attributed to the progress of a specific patterning technique, which is known as photolithography.



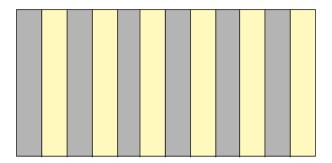
The p - n Junction

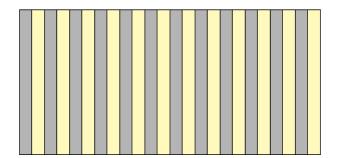




- A p—n junction is formed at the boundary between a p-type and n-type semiconductor.
- If two separate pieces of material were used, this would introduce a grain boundary between the semiconductors which severely inhibits its utility by scattering the electrons and holes.
- so p—n junctions are created in a single crystal of semiconductor by doping
- P-N junctions are elementary "building blocks" of many semiconductor electronic devices such as diodes, transistors, solar cells, and integrated circuits

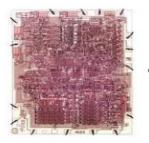
The p – n Junction

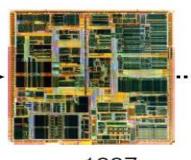


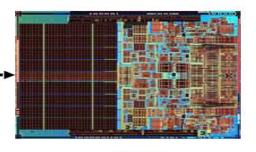


- So simply put if your lines become narrower, you can have more number of p n junctions on a chip whose physical dimensions are the same.
- These lines are created by the method of Photolithography.
- For example while a Pentium II processor had lines which are 300 nm wide, the lines are about 32 nm wide in a i-core 5 processor.
- Similarly progress in patterning is also responsible for higher capacity memories.

Intel Microprocessors – Brief History







1971 Intel 4004 µP 2,300 transistors 108 KHz 10 µm linewidth

1985 Intel 386 µP 275K transistors 33 MHz 1.5 µm

1997 Intel PII µP 7.5 M-transistor 300 MHz 0.25 µm

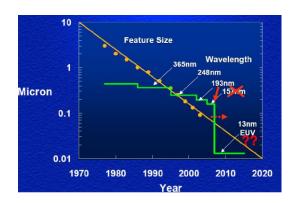
2006 Intel Core 2 Duo 291 M-transistor 2.4 GHz 0.065 µm

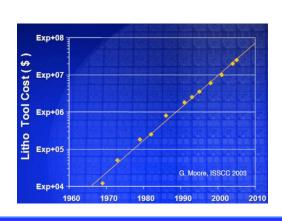
Historically, advances in microelectronics have been due to ability to making smaller and denser patterns.

- →Photolithography has been the workhorse of the semiconductor industry.
- → Lithography is key technology pacing Moore's Law



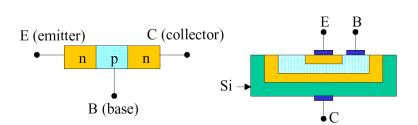


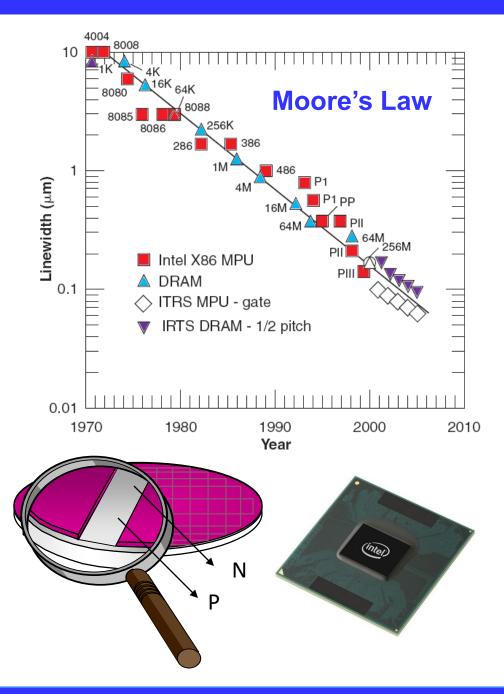




Photolithography

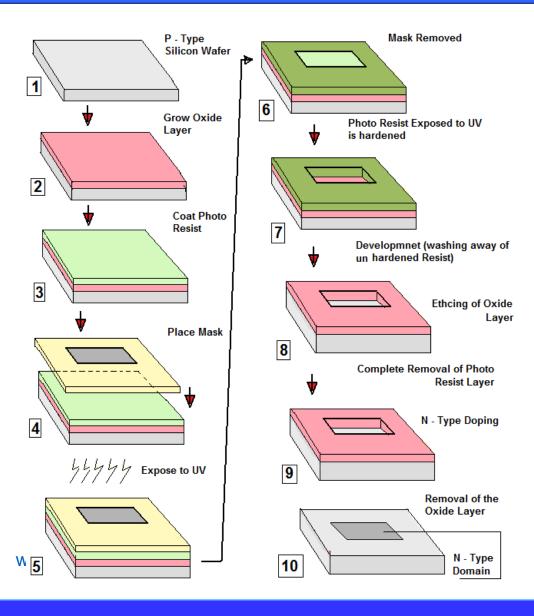
- Innovations in the integrated circuit industry is the main motive force for the tremendous advance in the field of surface patterning.
 - Transistor invented in 1947.
 - The first Integrated Circuit built in 1960. The line width in integrated circuits was 5 μ m.
 - First IBM PC (1981), 16 K Byte memory, 4.77 MHz clock speed.
 - Line widths of 350 nm was achieved, when 40 GB D-RAM was discovered in 1997.
 - Present state ~ 40 nm.
- Narrower is the line size, closer is the packing, better is the performance of the circuit!





Kharagpur

Photolithography Process: Basic Steps



Silicon Wafer

Photo resist

Spin Coating

Mask

Optical Source

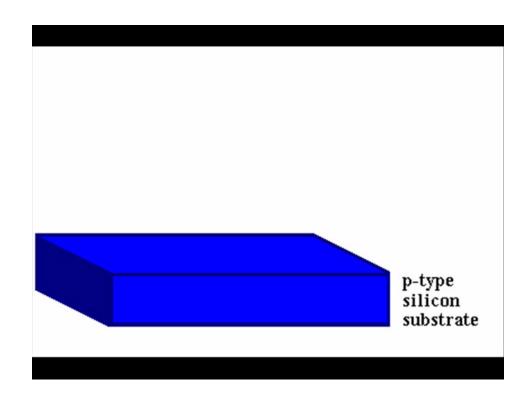
Mask Aligner

Developer

Etching

Photolithography Process: Basic Steps

- 1. Surface Preparation
- 2. Deposition of the Barrier Layer (SiO₂)
- 3. Photoresist Application
- 4. Soft Bake
- 5. Mask Align
- 6. Expose to UV
- 7. Develop
- 8. Hard Bake
- 9. Etch
- 10. Resist Strip



Wafer Cleaning

In the first step, the wafers are chemically cleaned to remove particulate matter on the surface as well as any types of organic, inorganic and metallic impurities.

Barrier Formation

A Silicon Surface has very high surface energy and oxidizes immediately in contact with air. This oxide layer is very thin. This silica layer itself cannot be used as a barrier. So, SiO2 layer is grown on the wafer at this stage.

Photo Resist Processing

Photo resist is coated on to the substrate by the method of spin coating, in most cases. It is possible to obtain films which are very thin (down to few nm) and are extremely smooth by the method of spin coating.

Photo Resist Processing

Consists of Six steps:

- 1) Dehydration and Priming
- 2) Resist coating
- 3) Soft baking
- 4) Exposure
- 5) Development and
- 6) Post-development inspection.

Photo Resist

It's a special class of Photo Sensitive Polymer.

Photoresist layers have two basic functions:

- 1) precise pattern formation; and
- 2) protection of the substrate from chemical attack during the etch process.

Typical resists consist of three components:

- 1) The resin, which serves as the binder of the film;
- 2) The inhibitor or sensitizer, which is the photoactive ingredient; and
- 3) The solvent, which keeps the resist in liquid state until it is processed.

Photo Resist

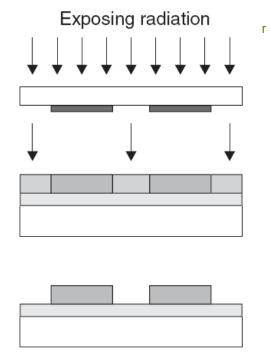
There are two different types of photo resists:

Positive and Negative. (Tones)

A Positive Photo resist when exposed to UV light undergoes structural changes (degradation) and becomes more soluble in the developer.

The exposed resist is then washed away by a developer solution.

An exact copy of the mask pattern is created on the resist layer (positive replica)



b) Positive photoresist

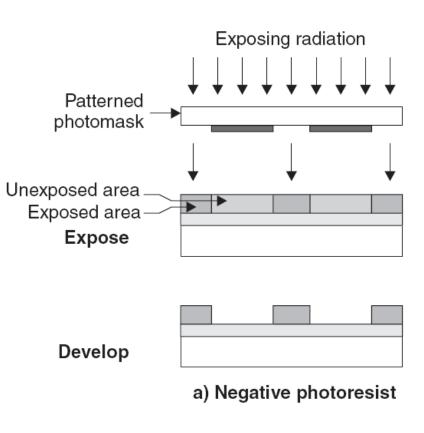
Photo Resist

A Negative Photo resist when exposed to UV light undergoes structural chang (polymerizes/ cross links) and become more less in the developer, as compare Unexposed area to the unexposed resist.

Patterned photomask Unexposed area Exposed area

When exposed, the resist which is not exposed to UV light gets washed away by a developer solution.

An inverse copy of the mask pattern is created on the resist layer (negative replica)



The First Commercial Photoresist was a Negative Photo Resist: Kodak Thin Film Resist

Photo Resist Processing

Consists of Six steps:

- 1) Dehydration and Priming
- 2) Resist coating
- 3) Soft baking
- 4) Exposure
- 5) Development and
- 6) Post-development inspection.

Dehydration and Priming

Before the resist is coated, the wafer must be free of moisture and contaminants, both of which cause a severe problem in resist processing.

Dehydration baking is performed to eliminate any moisture adsorbed on the wafer surfaces, as hydrated substrates lead to adhesion failures.

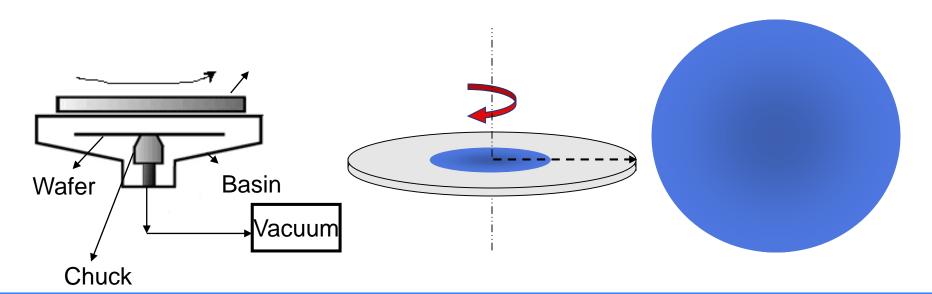
This is usually performed by heating to temperatures between 400 °C to 800 °C.

After dehydration baking, the wafer is coated with a pre-resist priming layer which enhances the adhesion properties of the wafer.

One of the most common primers used for this purpose is hexamethyldisilazane (HMDS). Resist coating must follow as soon as possible after priming

Spin Coating

- A process in which solution is spread evenly over a surface using centripetal force.
- Spin coating will result in a relatively uniform thin film of a specific thickness.
- Spin coating is an important way of creating thin films in the microelectronics industry.



Different Steps of Spin Coating

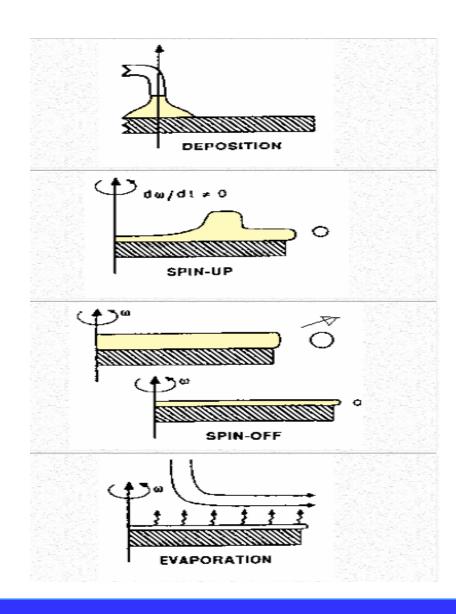
Dispense the Polymer Solution

Stage 1:

Meniscus traveling From Centre to Edge

Stage 2: Splash Drainage From the Edges

Stage 3: Evaporation dominated Drying



Parameters Affecting Film Thickness in Spin Coating

Spin Speed (RPM)

Spin Coating is followed by Edge Bead Removal

Dispensed drop volume

Choice of Solvent

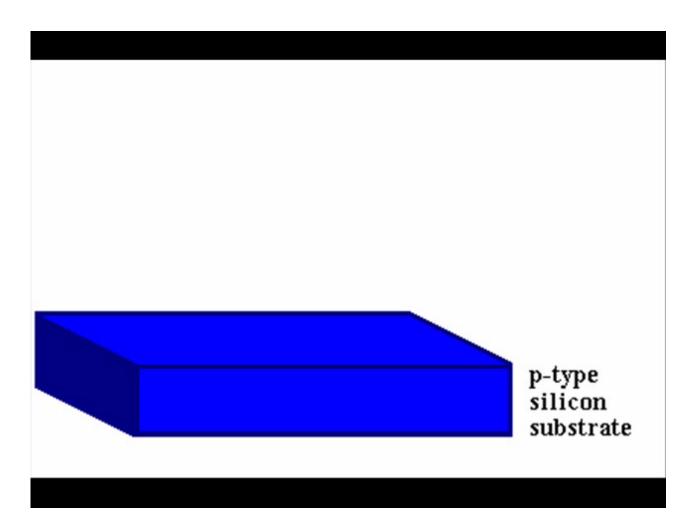
Duration of Spinning

Ambient Condition

(which in turn affects the solvent evaporation rate)

Photolithography Process: Basic Steps

- 1. Surface Preparation
- 2. Deposition of the Barrier Layer (SiO₂)
- 3. Photoresist Application
- 4. Soft Bake
- 5. Mask Align
- 6. Expose to UV
- 7. Develop
- 8. Hard Bake
- 9. Etch
- 10. Resist Strip

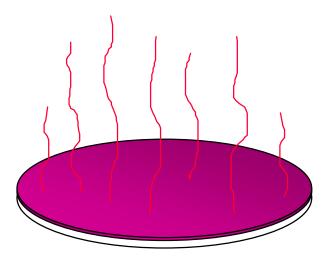


After spin coating, the solvent content in the as cast film drops to around 10 - 20%.

The remnant solvent has to be removed before exposure, which is achieved during the stage of Soft Baking.

The photoresist coatings become photosensitive, or imageable, only after soft-baking.

- Improves adhesion
- Improves uniformity
- Improves etch resistance
- Improves linewidth control
- Optimizes light absorbance characteristics of photoresist



Temperature: 90 -110 °C

Soft Baking

Over soft-baking will degrade the photosensitivity of resists by either reducing the developer solubility or actually destroying a portion of the sensitizer.

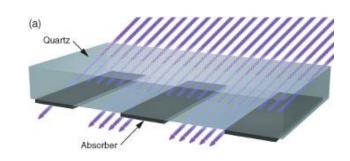
Under soft-baking will prevent light from reaching the sensitizer. Positive resists are incompletely exposed if considerable solvent remains in the coating.

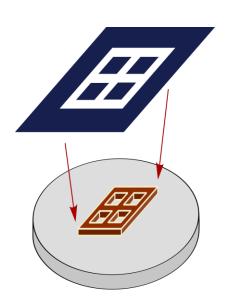
A under soft-baked positive resists is readily attacked by the developer in both exposed and unexposed areas, causing less etching resistance

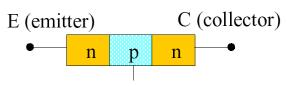
Photo Mask

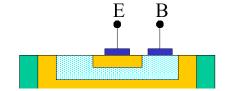
A photomask is an opaque plate with holes or transparencies that allow light to shine through in a defined pattern

- Lithographic photomasks are typically transparent fused silica blanks covered with a pattern defined with a chrome metal absorbing film.
- Use e-beam or laser or x-ray to strip off chromium
- For Integrated Circuits, multiple masks with multiple pattern are necessary.





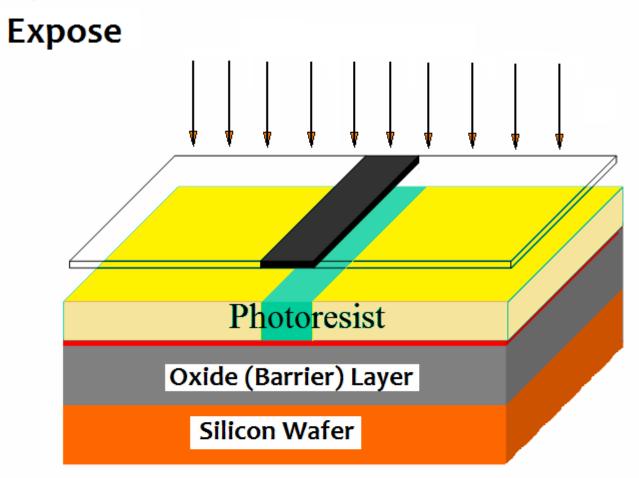




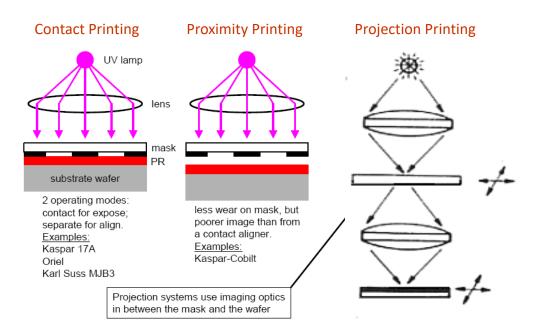
Mask Aligners:

- Almost any microscale device or structure requires more than one photomask step.
- The job of the aligner is to allow its user to align features on a substrate (wafer) to features on a photomask.
- The production of sophisticated electronic devices may involve ten or more of these alignment steps.

Mask Aligner



Optical Exposure: Printing Modes



Proximity printer resolution versus gap.

Gap (μm)	Resolution (μm)
10	1.47
15	1.77
20	2.03
30	2.46

Contact Printing

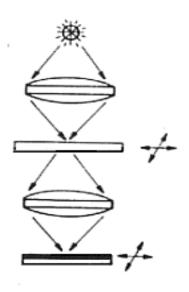
- The resist-coated silicon wafer is kept at physical contact with the photomask during exposure.
- Because of the contact between the resist and mask, very high resolution is possible in contact printing (e.g. 1-micron features)
- The problem with contact printing is that debris, trapped between the resist and the mask, can damage the mask and cause defects

Proximity Printing

- The proximity exposure method is similar to contact printing except that a small gap ~ 10 to 25 microns, is maintained between the wafer and the mask during exposure.
- This gap minimizes (but may not eliminate) mask damage. Approximately 2- to 4-micron resolution is possible with proximity printing

Projection Printing or Alignment

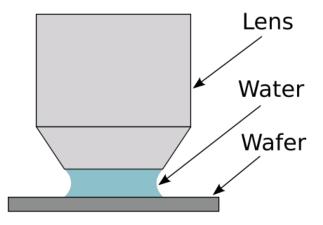
Projection Printing



Projection Printing

- Projection printing, avoids mask damage entirely.
- An image of the patterns on the mask is projected onto the resistcoated wafer, which is many centimeters away.
- •In order to achieve high resolution, only a small portion of the mask is imaged.
- This small image field is scanned or stepped over the surface of the wafer.
- Projection printers that step the mask image over the wafer surface are called step-and-repeat systems.
- Step-and-repeat projection printers are capable of approximately 1-micron resolution.

Most present day photo lithography instruments work on this principle



Immersion Lithography

A photolithography 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 RI of the liquid.

Enhancement in Numerical Aperture

Post Bake

Post bake is performed after exposure, at temperatures slighly higher than soft bake.

Developing

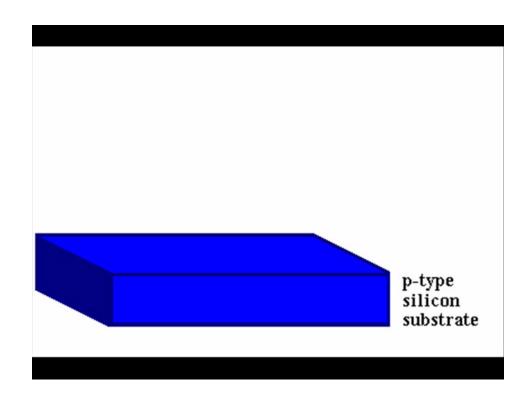
This step a special solvent is used to wash the exposed/un-exposed photo resist layer, resulting in the patterns on the PR layer.

Hard Bake

Final baking step to increase stiffness of the patterned photo resist layer and increase adhesion as well

Photolithography Process: Basic Steps

- 1. Surface Preparation
- 2. Deposition of the Barrier Layer (SiO₂)
- 3. Photoresist Application
- 4. Soft Bake
- 5. Mask Align
- 6. Expose to UV
- 7. Develop
- 8. Hard Bake
- 9. Etch
- 10. Resist Strip



Photolithography: Limitations

- (1) It requires expensive instruments and facilities with high capital investment
- (2) The pattern resolution is limited by optical diffraction
- (3) The method is not suitable for patterning all types of polymers, and only photosensitive resist materials (photoresists) can be directly patterned
- (4) The technique requires harsh processing conditions such as exposure to UV radiation, chemical etching, and so on, and therefore has limited application for sensitive materials such as biological samples with living cells
- (5) the method cannot be easily applied for patterning of nonplanar or curved surfaces