Lecture 8

Photoresists and Non-optical Lithography

Reading:

Chapters 8 and 9 and notes derived from a HIGHLY recommended book by Chris Mack, "Fundamental Principles of Optical Lithography". Any serious student interested in a career in the semiconductor industry or lithography should consider this book as a must read.

Photoresist “Chemistry” (ECE style)

Photoresists generally consist of 3 parts:
1.) Resin: “plastic like” or “glue-like” compound that is solid in it’s undiluted state (Novolac -plywood example).
2.) Solvent: Chemicals used to dissolve the resin, allowing the resin to be applied in a liquid state.
3.) Photoactive Compound (PAC): Act to inhibit or promote the dissolution of the resin in the developer. PAC inhibits dissolution in positive resists before light exposure. After exposure the PAC promotes dissolution of the resin.

Photoresists are constructed from complex hydrocarbon chains known as polymers. Polymers are chains of smaller molecules known as monomers. Polymers are the basis of LCD displays, plastic tubing like PVC, acrylic, simulated leather.

Polymers have the ability to form long chains with many branches as shown in Figure 8-3.

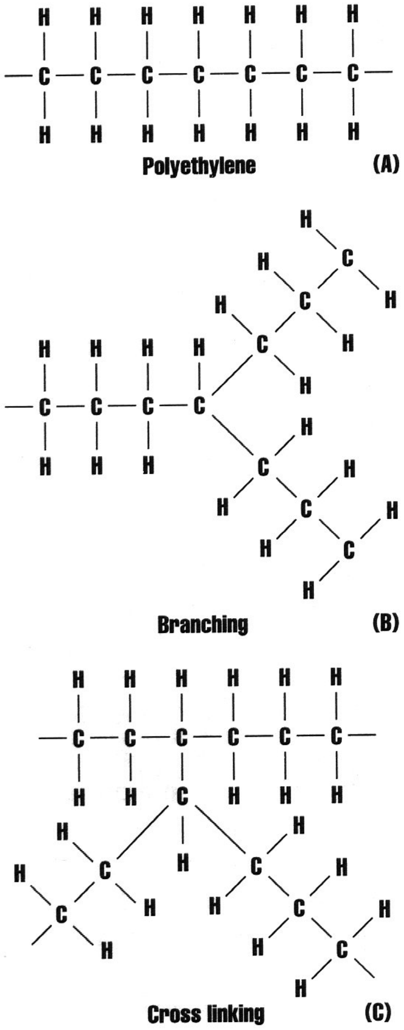


Figure 8-3 (a) Polyethylene, an example of a simple polymer. (b) Branch chain polymers, (c) Cross linking.

Positive Photoresist "Chemistry" (ECE style)

Most positive resists are based on Diazoquinones (DQ) or Diazonaphthoquinone (DNQ).

1.) Start with a DQ molecule (R is a manufacturer variation). The DQ molecule will not dissolve in a base developer solution (pH >7).

2.) UV light breaks the nitrogen molecule off forming an unstable molecule.

3.) To "stabilize" itself, one of the 6 carbon atoms in the ring pops out of the ring (leaving 5).

4.) Once the solution is exposed to water (a developer/water mixture), an OH group attaches to the carbon atom, forming an acid.

5.) The acid can then react and dissolve with the basic developer solution.

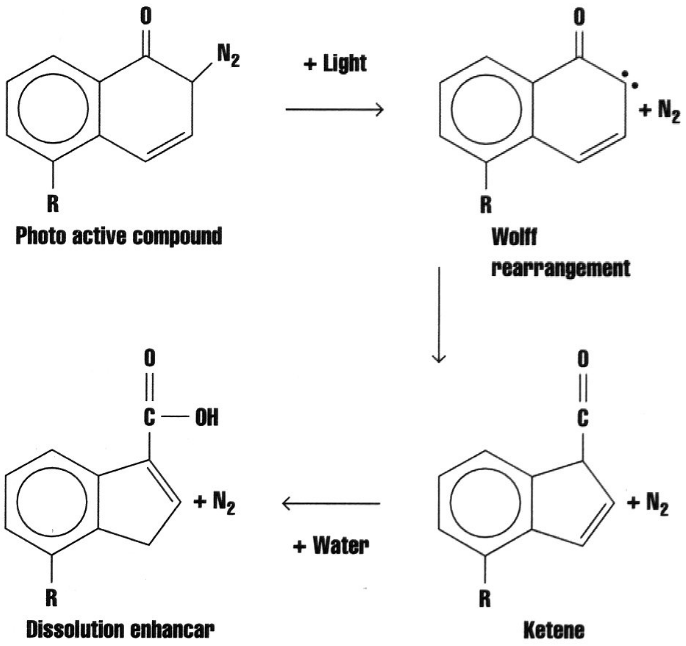


Figure 8-6 Photolysis and subsequent reactions of DQ upon UV exposure.

Measures of Resist Contrast

Just as the MTF is a measure of the exposure tool's ability to vary the intensity of light, a PR is characterized by it's ability to distinguish between light and dark portions of a mask.

2 measures of Contrast:

1.) Contrast (γ)
2.) Contrast Modulation Transfer Function (CMTF)

1.) Contrast (use figure 8-7),

$$\gamma = \frac{1}{\log_{10}\left(\frac{D_{100}}{D_0}\right)} = \frac{1}{\beta + \alpha T_{resist}}$$

where α is the absorption coefficient of the resist (1/length) and T_{resist} is the resist thickness and β is a constant for the resist.

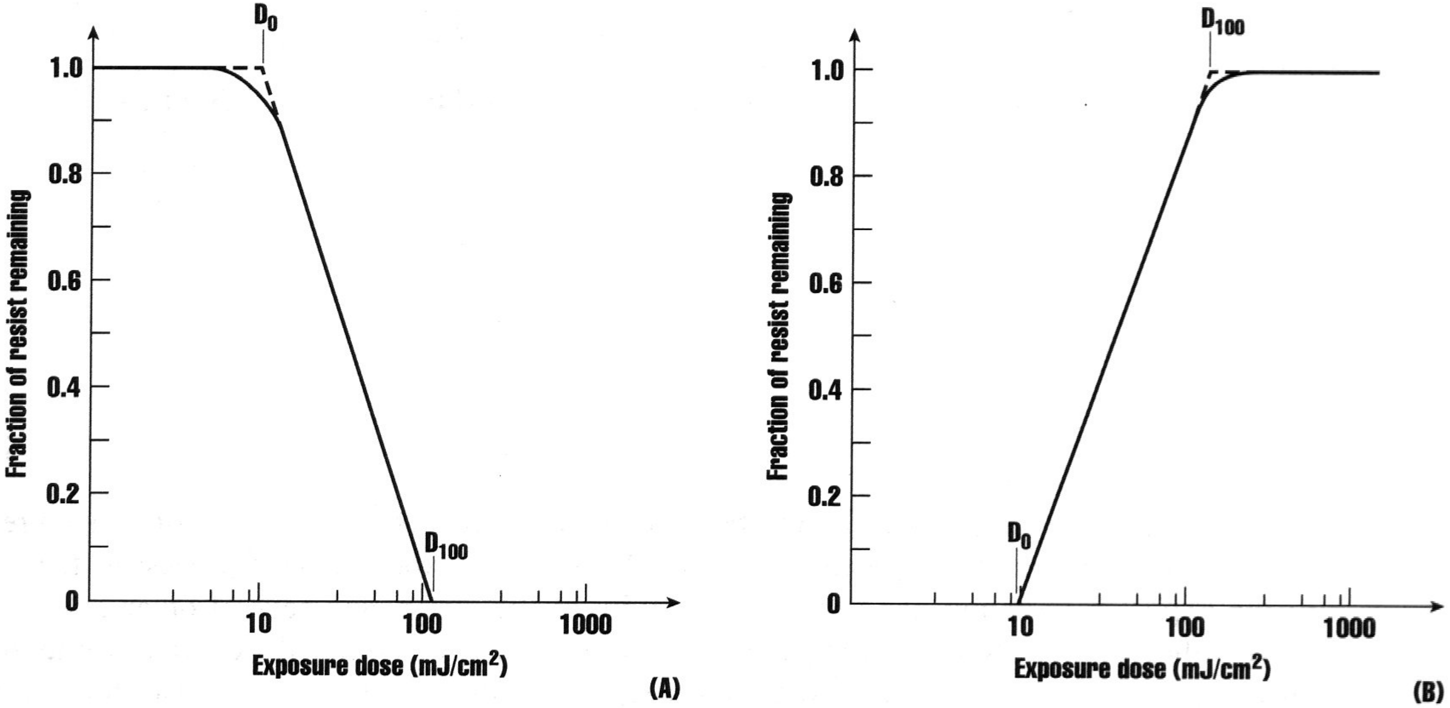


Figure 8-7 Contrast curves for idealized resists: (a) positive tone and (b) negative tone.

Measures of Resist Contrast

2.) CTMF = Approximately the minimum tool modulation transfer function resulting in a pattern being transferred to the resist.

$$CTMF_{resist} = \frac{D_{100} - D_0}{D_{100} + D_0} = \frac{10^{1/\gamma} - 1}{10^{1/\gamma} + 1}$$

If the areal image MTF is less than the photoresist CTMF, the image is not transferred.

Other issues with PR/Lithography:

Index of refraction, n, can enhance resolution (similarly to immersion lithography) but unfortunately, n is generally fairly close to 1. In general, the Index of refraction is described by the Cauchy equation,

$$n(\lambda) = A + \frac{B}{\lambda^2} + \frac{C}{\lambda^4} + \cdots,$$

…but these parameters are a function of exposure, and thus depth. This depth dependence is called "bleaching" (discussed below).

Optical Processes in Photoresist

The intensity at each position in the resist depends on how much light is absorbed above it and is complicated by the absorption coefficient, α, being a function of depth, α(z), and total optical dose (Watts/cm^2 x Time):

$$I(z) = I_o e^{-z\alpha(z)}$$

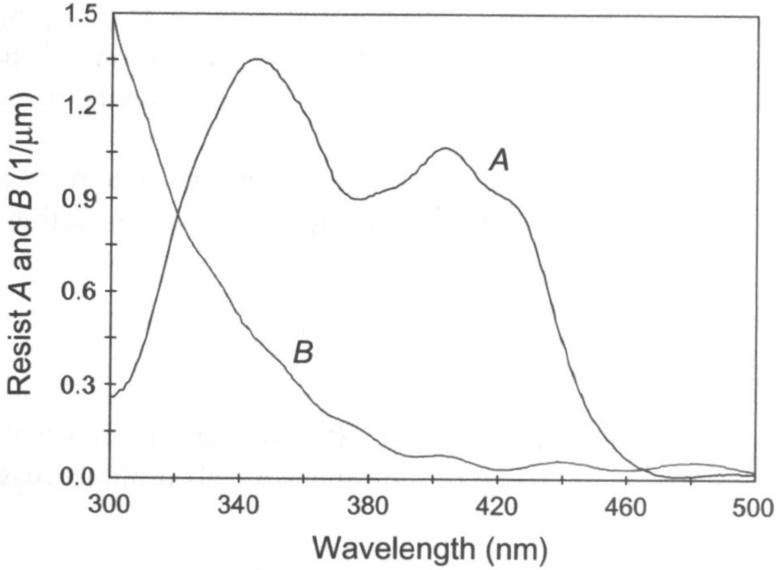
Since α(z) depends on the optical dose, one can break the absorption coefficient up into components that change with dose (photoactive compounds that change chemistry and thus absorption with exposure) and absorption compounds that are not light sensitive (time invariant).

$$\alpha(z) = Am + B$$

$$where \quad m = \frac{M}{M_o}$$

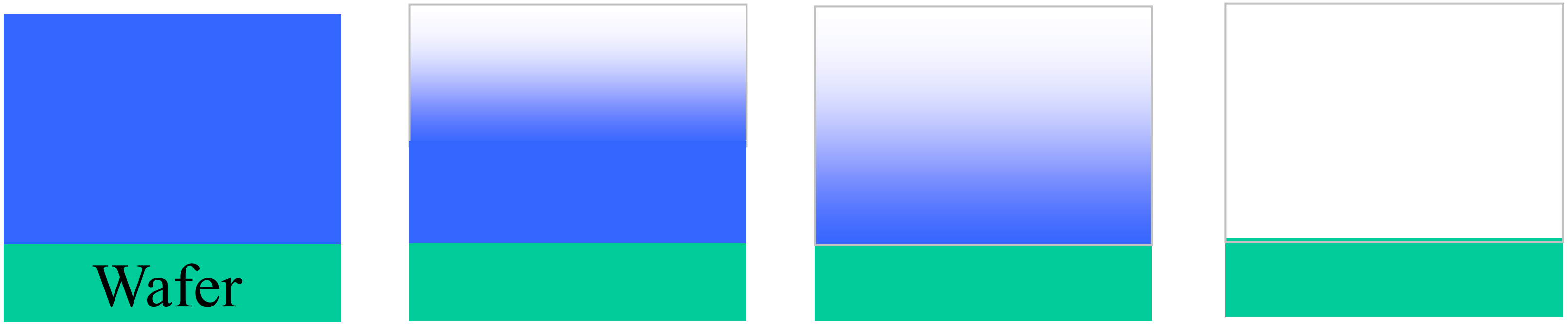
m is the fraction of photosensitive material with concentration, M, that has not been reacted by the light and Mo is the initial concentration of the photosensitive material.

A and B are known as the bleachable and non-bleachable absorption coefficients and the 1st two of 3 Dill parameters. Positive A values indicate the photoresist gets more transparent when exposed whereas a negative A indicates a photoresist that becomes more opaque with exposure.



Optical Processes in Photoresist

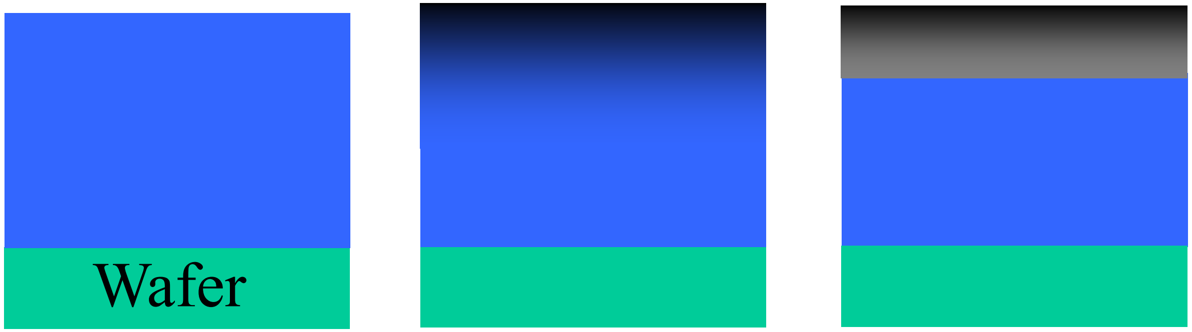
Positive A resist:



Increasing Time →

Bleaching leads to a uniform exposure with the entire resist evenly exposed.

Negative A resist:



Can be used to achieve higher resolution than normally possible with a thick resist since only a thin skin is exposed emulating a thinner resist.

Increasing Time →

Optical Processes in Photoresist

The third Dill parameter, C, describes the time rate of conversion of the photosensitive material.

$$\frac{dm(z)}{dt} = -Cm(z)I(z)$$

$$m(z) = e^{-C\,t\,I(z)}$$

The rate of consumption of the photoactive compound is proportional to the intensity of the light. C is the proportionality constant and determines the time needed for exposure (i.e. is related to the sensitivity of the resist).

Where several assumptions are made in solving this differential equation and (I) x (t) is the optical dose. If D is the resist thickness, the Dill parameters can be measured by:

$$A = \frac{1}{D}\ln\left(\frac{T(\infty)}{T(0)}\right) = \alpha_{unexposed} - \alpha_{exposed}$$

$$B = -\frac{1}{D}\ln\left(\frac{T(\infty)}{T_{12}}\right) = \alpha_{exposed}$$

$$A + B = \alpha_{unexposed}$$

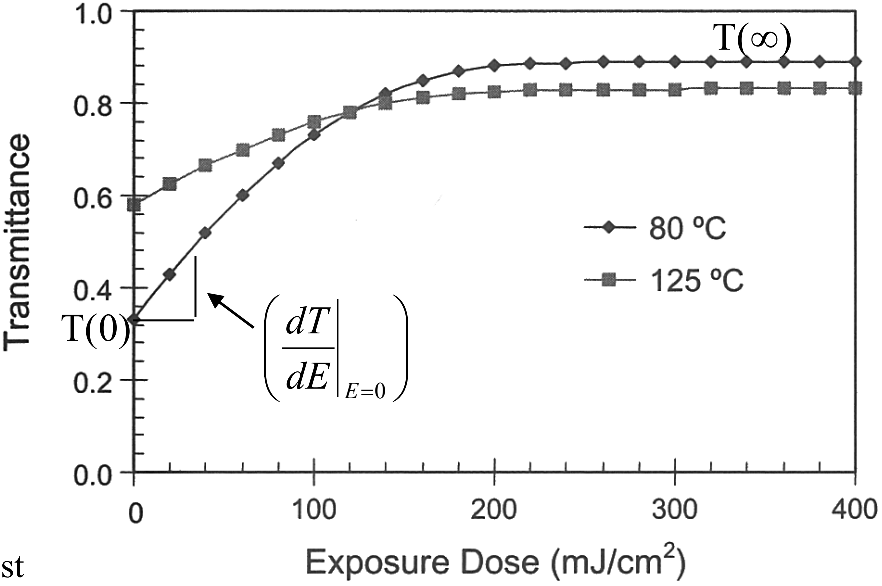
$$C = \frac{A+B}{AT(0)[1-T(0)]T_{12}}\left(\left.\frac{dT}{dE}\right|_{E=0}\right)$$

$$T_{12} = 1 - \left(\frac{n_{resist}-1}{n_{resist}+1}\right)^2 \text{ is the air - resist interface,}$$

T(0) is the transmittance of the unexposed resist, and

$T(\infty)$ is the transmittance of the completely exposed resist

$\left(\left.\frac{dT}{dE}\right|_{E=0}\right)$ is the initial slope of the transmittance vs dose curve

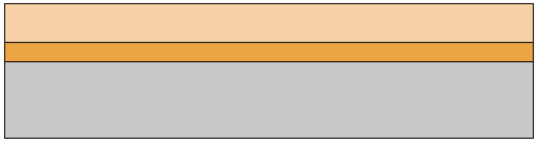


For a full discussion of all Photolithography processes including detailed chemistry, general solutions with minimal assumptions, see an excellent book by Chris Mack entitled *Fundamental Principles of Optical Lithography*

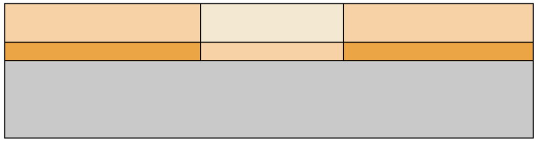
Using Two Layer Resists combined with Bleaching to Enhance Lift Off

Using a low bleaching top resist in combination with a "negative A" bleaching resist (Lift Off Resist or LOR) below it can result in a "reentrant profile" useful for creating a cliff in lift off processes.

1. Coat and prebake LOR

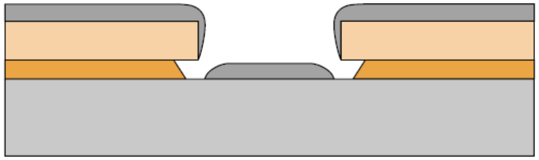


2. Coat and prebake imaging resist

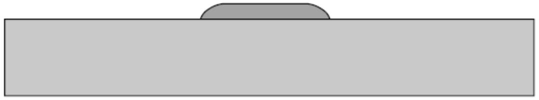


3. Expose imaging resist

4. Develop resist and LOR. LOR develops isotropically, creating a bi-layer reentrant sidewall profile



5. Deposit film. The reentrant profile ensures discontinuous film deposition.



6. Lift-off bi-layer resist stack, leaving only desired film.

Photoresist Issues

Resist Application:

- Resist thickness varies as:

$$\text{Resist Thickness} \propto \frac{1}{\sqrt{\varpi}}$$

where ω is the spin speed.

- Resist can "pile up" at the wafer edge making contact lithography non-uniform.

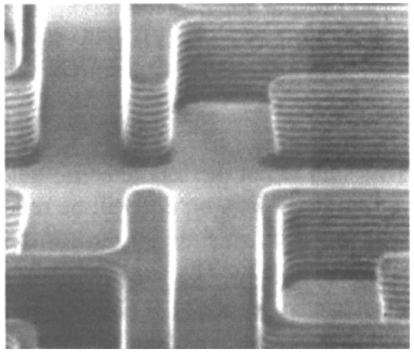
  You can spin on the resist and pre-expose/dissolve this "beaded up" area to remove it before proceeding with pattern transfer. Alternatively, some spinners have an edge bead removal solvent that is sprayed locally on the wafer edge to remove the edge bead.

Amplified Resists:

- Much more complex resists primarily used to increase throughput by minimizing the dose (time) required for exposure. These are also used for Deep UV resists that have poor sensitivity (small C).
  - UV light does not significantly weaken the resist but instead generates acids that upon post exposure bake act as catalysts to strengthen (or weaken) the resist.
  - Since each acid molecule can react (strengthen or weaken) multiple polymer chains, less light is needed.

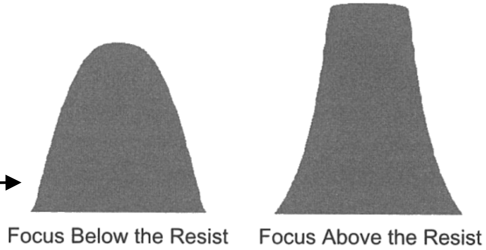
Standing Waves in Resists:

- Front to back surface (substrate) reflections in resists can create standing wave patterns that alter scallop the resist edges as shown below.



Focal Point

- Focal point effects resist shape as shown to the right



Photoresist Issues

Step coverage and Planarization:
Polymers such as Polymethyl methacrylate (PMMA) or spin on or deposited oxides are used to "planarize" the wafer after previous patterning (metal lines, gate oxide definitions, etc…) allowing higher resolution (limited depth of field) lithography.

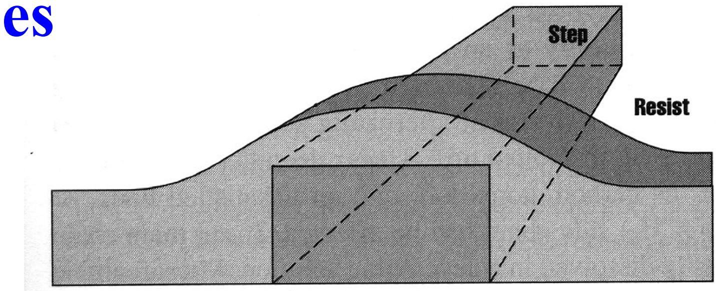
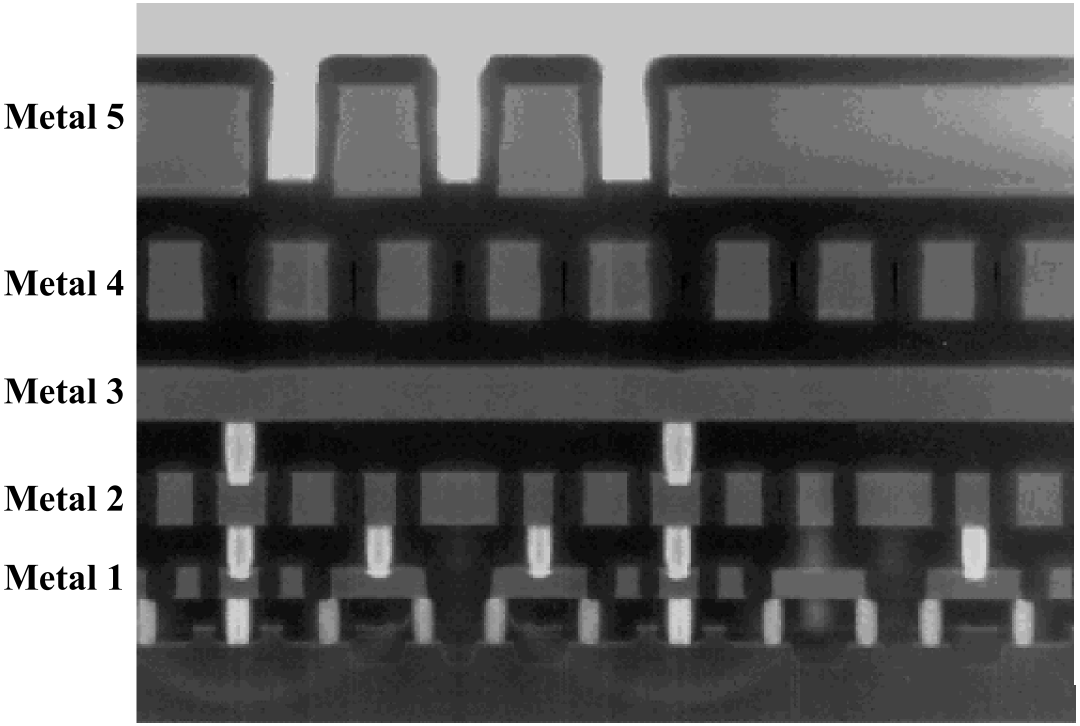
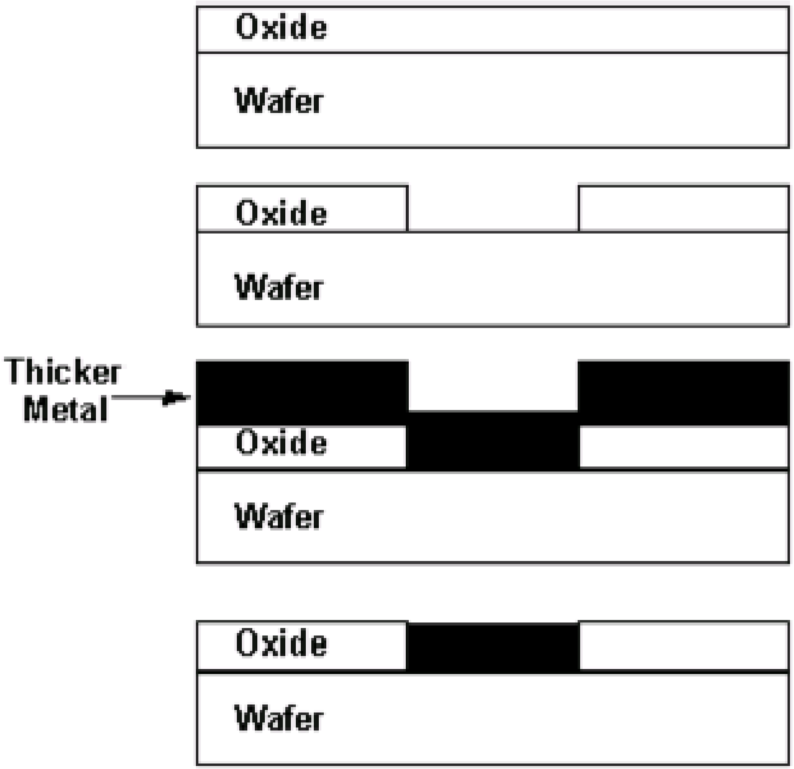


Figure 8-14 Cross-sectional view of resist as it covers a vertical step.

Damascene processing is currently being employed: (Named after an art form from the Damascus Syria area).
Provides for a means of having very flat wafers even after previous patterning steps. Allows for very high resolution lithography with limited depth of field.



The cross-section of 5 interconnect-level structure in Pentium II©



Damascene Process

Single Damascene:

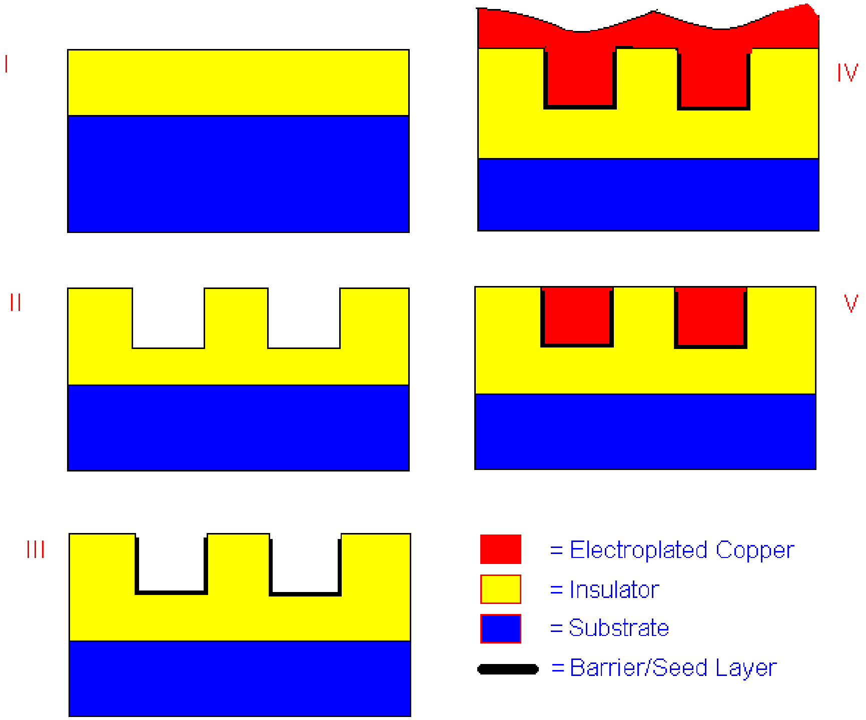
I.) Deposit dielectric layer (CVD dielectric, spin on, etc…)

II.) Etch via or trench structure

III.) CVD deposit a diffusion barrier and/or a metal seed layer for the subsequent step. Deposition rate is slow

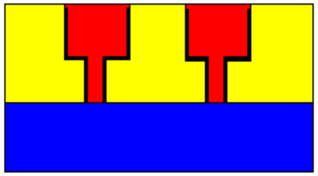
IV.) Electroplate (or sputter) the metal. Electroplating consists of an electrochemical reaction that takes metal dissolved in an acid solution and deposits it rapidly on the patterned wafer. Physical vapor deposition (sputtering or evaporation) is sometimes substituted for this step.

V.) Polish the combined structure to a flat surface.



Dual Damascene:

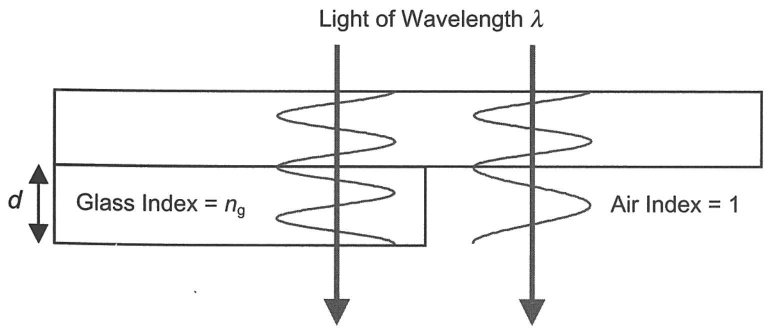
Similar process, but the "contact via" (for making connections from various interconnect layers) and the metal lines (used for connecting devices/circuits within a single layer) are lithographically defined and etched in two separate steps.

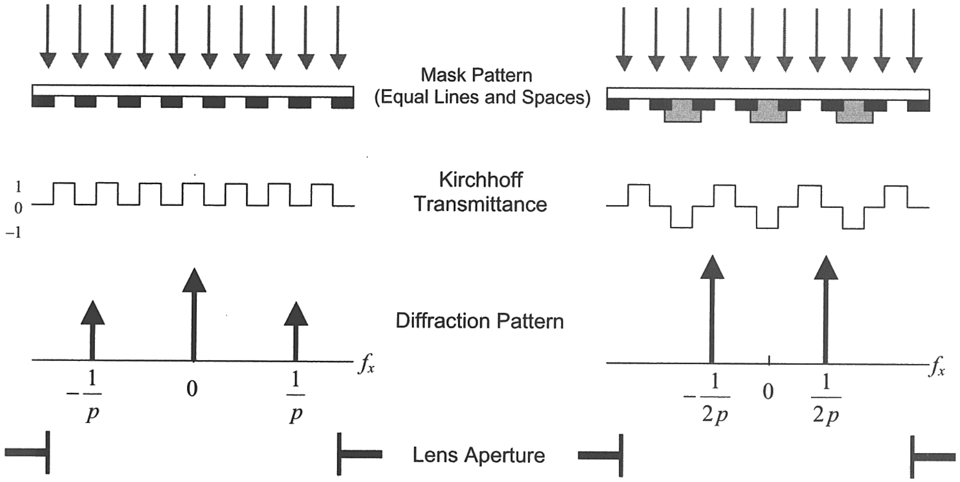


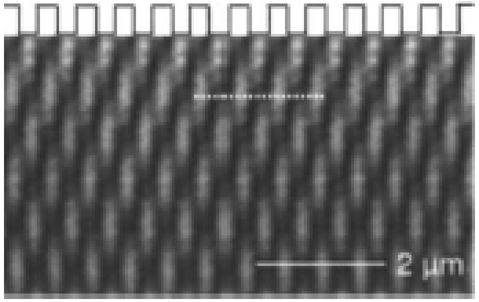
Figures for this page provided by student term paper "Copper Interconnect Technology", W.C. Bouverie, ECE 6450, 11/30/99

Advanced Lithography

Phase Shift Lithography uses various thicknesses of variable index or thickness material near the feature to be imaged. Using advanced calculations, constructive/destructive interference can result in a sharper areal image.







Actual optical intensity under a mask measured with NSOM from Maria et al,

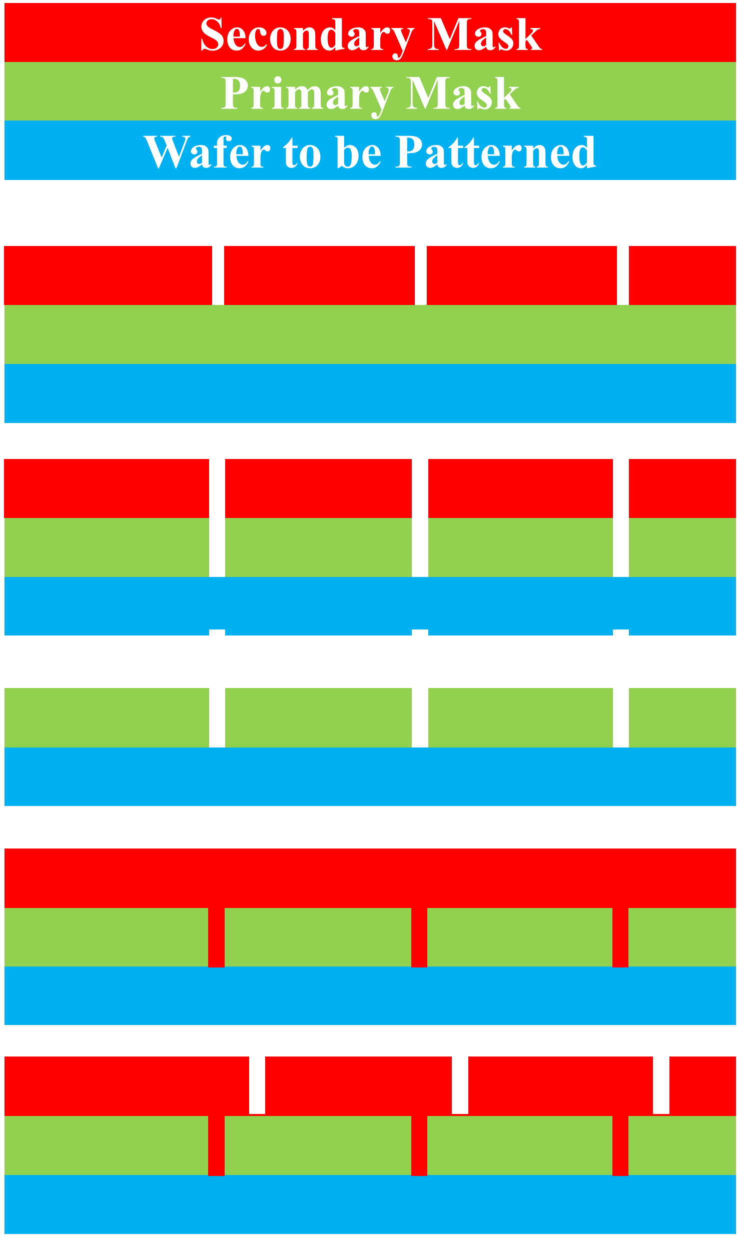
J. Vac. Sci. Technol. B, Vol. 24, No. 2, Mar/Apr 2006

Advanced Lithography

Multiple Exposures and Multiple Etches using spatial mask shifts can print smaller features than the optical pitch of the inherent stepper.

Many patterns (DRAM for example) are very repetitive but require features that are smaller than the tool can generate. Using a Mask shift (which can be very precise) remarkably small features can be implemented.

Shown here is the Double expose, double etch process.

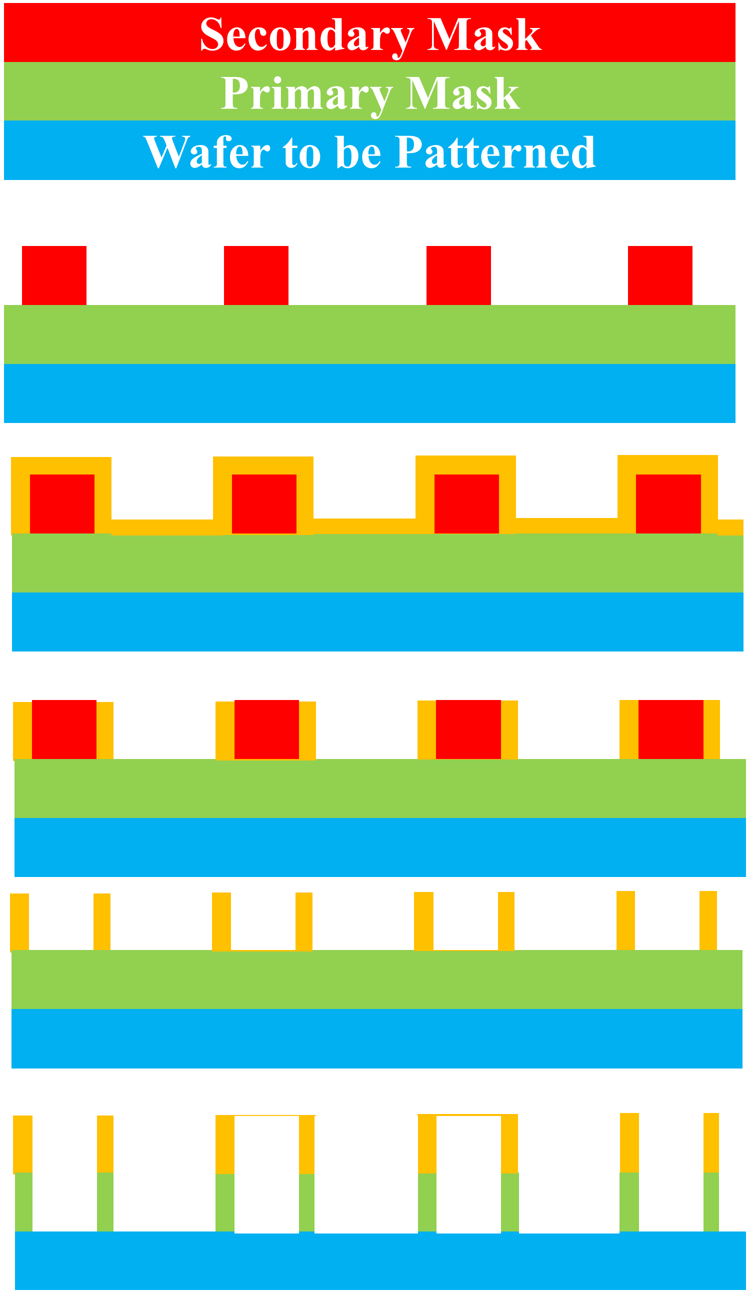


- Expose 1
- Etch 1
- Etch 2nd Mask
- Apply 2nd Mask Again
- Expose 2

- Etch 2

- Etch 2nd Mask to result in Final Mask

Advanced Lithography



Sidewall Lithography uses asymmetric etch of thicker sidewalls compared to the over layers to print smaller features than the optical pitch of the inherent stepper

- Pattern Secondary Mask
- Conformal coating a 3rd Mask
- Directionally Etch 3rd mask just long enough to remove field regions leaving sidewalls
- Etch 2nd Mask
- Etch 3rd Mask to result in Final Mask

- Etch Primary Mask

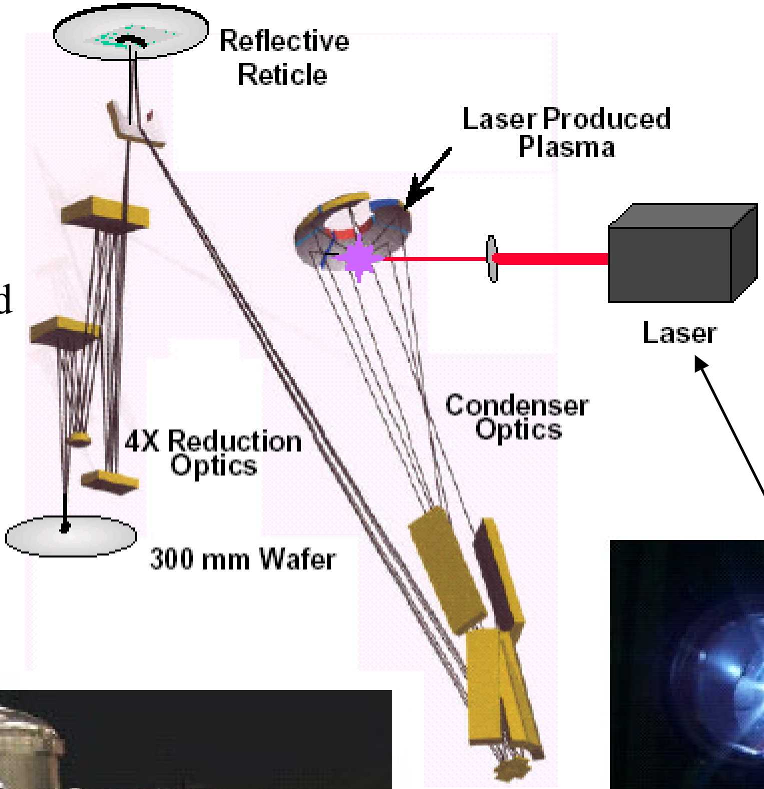
Advanced and "Future" (Here Now) Lithography

Since the minimum feature size is kλ/NA, the long term solution to obtaining smaller device sizes is to lower λ.

Changes must be made in current systems:

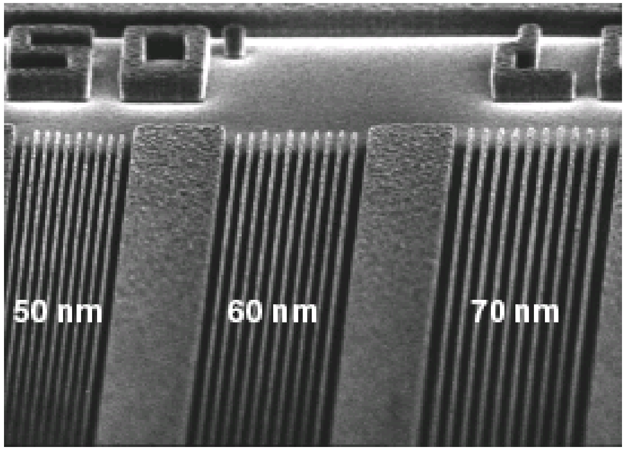
- Efficient small wavelength sources must be developed
- Reflective optics and masks must be developed
- Resists responsive in the extreme UV range must be developed
- Cost issues must be addressed

•2021 Samsung is using EUV in production of 7 nm DRAM



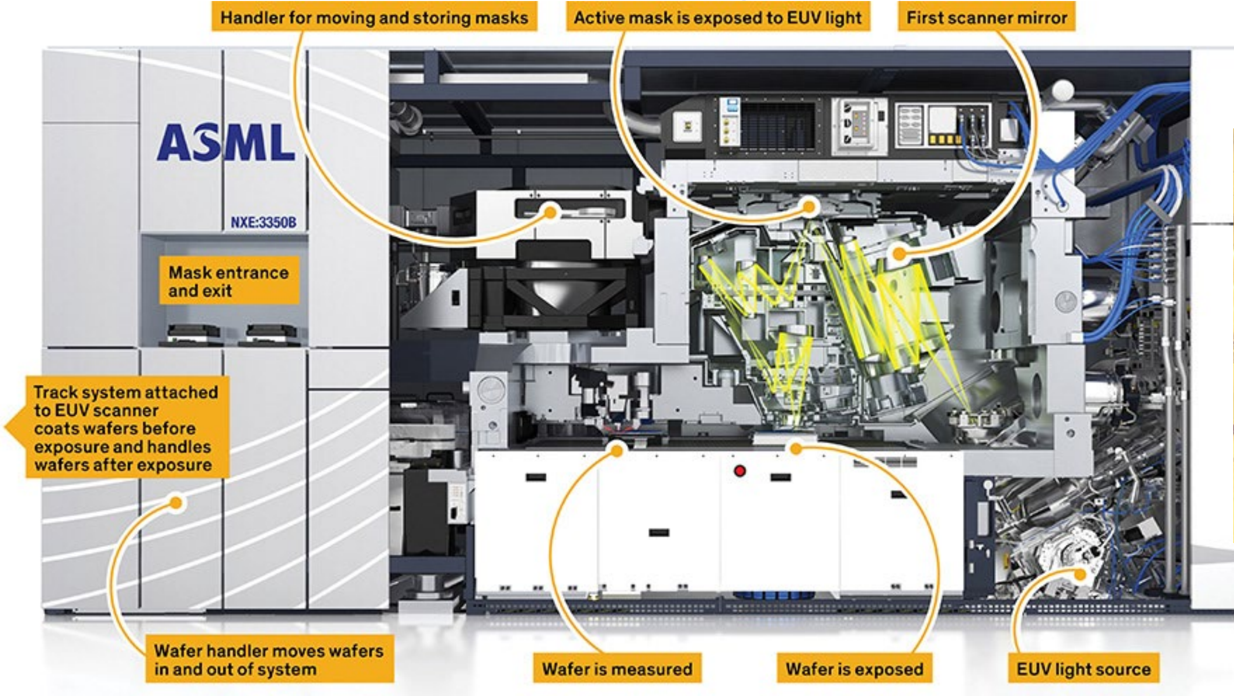
Extreme Ultraviolet Lithography

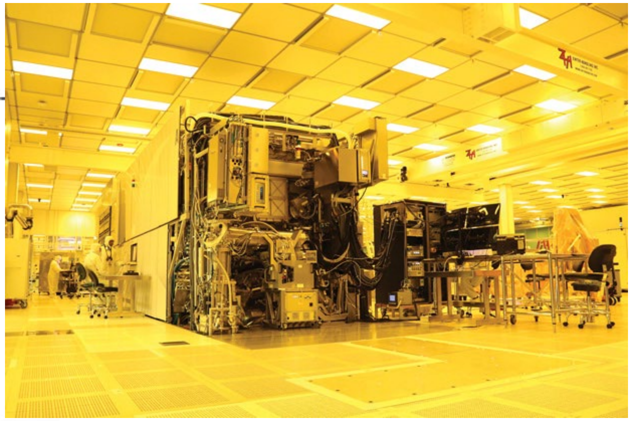
- 13.4 nm wavelength
- Use for 70 nm ~ 2005 timeframe



Figures extracted from Cahners MDR Microprocessor Forum 2000, October 11, 2000, Xtreme Semiconductor Process Technology, Charles (Chuck) W. Gwyn, Program Director Intel Corporation & EUV LLC

Updated Status: EUV Lithography is Here But being Adopted Slowly





Advanced EUV Stepper

Advanced and Future Lithography

Other companies/universities are taking the approach of using X-Rays or Electrons for low volume lithography:

X-Rays:

Advantages:

- Very small wavelength (1.5 Angstroms or shorter)
- Can be performed in air, but particles are a problem

Disadvantages:

- Bright sources of X-rays exist, but are still not bright enough for high throughput.
- Polished mirrors are very difficult and expensive to make and maintain.
- Shares all of EUVL problems.

Electron Beam Lithography:

Advantages:

- Extremely small wavelength (<0.01 Angstroms or shorter)
- Viable solutions for 5 nm features are available TODAY.
- No mirrors required.
- Limited need for optics.

Disadvantages:

- Small throughput (scanning)
- Even though small features can be directly written, it often has large pitch due to intense sidelobes from diffraction.
- Bright sources of do not exist resulting in very limited throughput.
- Vacuum based technology.