# ECE 416/516
# IC Technologies
# Lecture 8:
# Photoresist

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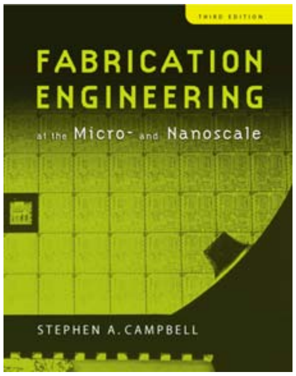
Spring 2012

## Chapter 8

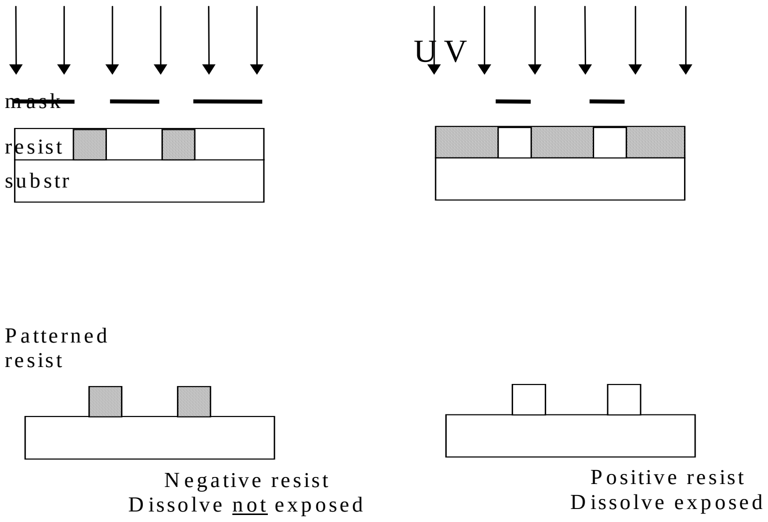
## Photoresists



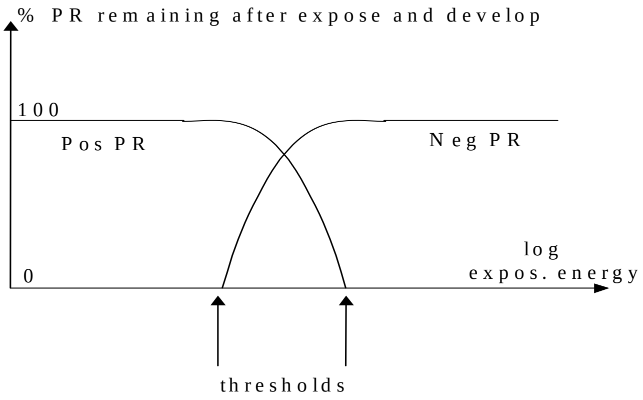
# Lecture Topics

- Lecture Topics
  - Positive and Negative Photoresists
  - Spin Coating Thickness
  - Spin Coat Planarization
  - Mask Registration
  - Effect of Dirt on Yield
  - Photoresist Exposure Contrast
  - Photoresist Development Rate
- Lecture Objectives
  - Can design process for pos or neg PR
  - Can calculate spin thickness
  - Can estimate planarization, defect yield
  - Can explain exposure contrast
  - Can calculate development rates

# Positive/Negative Photoresist



# Photoresist Exposure



Positive PR MORE soluble in developer after exposure

Negative PR LESS soluble in developer after exposure

# Exposure Notes

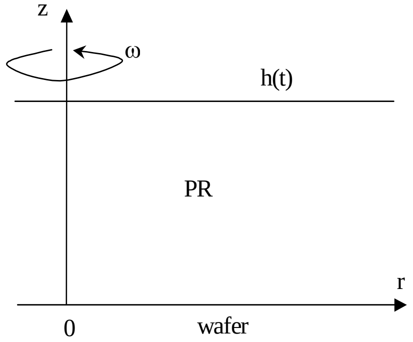
Curves depend on:
- PR thickness
- Exposure radiation
- Spectral response
- Development time
- Pre-bake? (improves adhesion)

Good Adhesion required for wet etch
- Etches under PR
- No problem with dry etch

Safe light -> $\lambda > 500$nm (yellow)

- typical UV resists insensitive to $\lambda > 500$nm

# PR Spin Coating #1



Laminar Flow

Uniform Pressure in film

Viscosity >> inertia

∴ Navier-Stokes equation

$$\mu\,(\partial^2 v_r/\partial z^2) = -\,\rho\,\omega^2 r,$$

where $\mu$, $\rho$ = liquid viscosity, density

Material balance -> $\partial h/\partial t = -r^{-1}\,[\partial(rq)/\partial r]$,

where $q = {}_0\!\int^h v_r\,dz$ = volumetric flow rate

# PR Spin Coating #2

Boundary Conditions:

- No slip at wafer surface, $v_r = 0$ at $z = 0$
- No shear stress at free surface,

  $dv_r/dz = 0$ at $z=h(r, t)$

Gives $v_r = (\rho\omega^2 r/2\mu)\,h^2(t)\,\{1 - [1 - z/h(t)]^2\}$

& $q = (\rho\omega^2 r/3\mu)\,h^3(t)$

& $\partial h/\partial t + (\rho\omega^2/3\mu)\,r^{-1}\,\partial(r^2h^3)/\partial r = 0$

Solution for $h = h_0$ at $t = 0$:

$h(t) = h_0/[\,1 + (4\rho\omega^2/3\mu)\,h_0^2 t\,]^{1/2}$

ie. uniform thickness if initially uniform

Also for $h \ll h_0$ (ie. long times) get :

$h(t) \approx (3\mu/4\rho)^{1/2}\,\omega^{-1}t^{-1/2}$ independent of $h_0$

Planarization

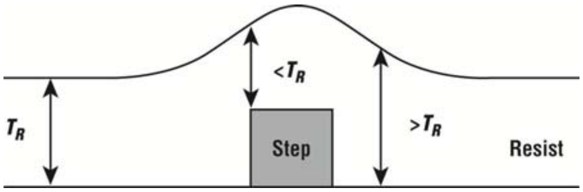
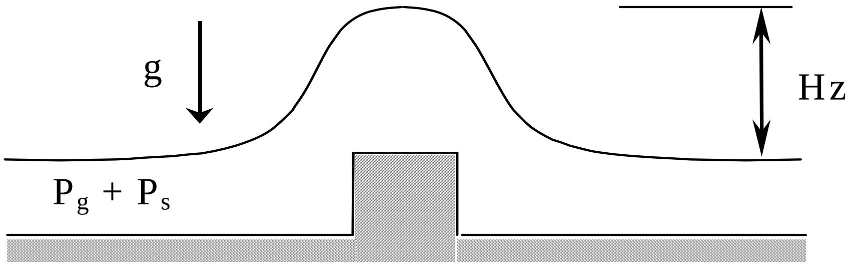


**Figure 8.14** Cross-sectional view of resist as it covers a vertical step.

Hence planarization may be necessary

## PR Planarization #1

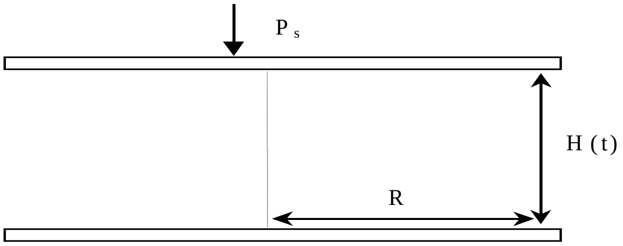


Hydrostatic pressure $P_g = \rho g H_2$ due to gravity

Interfacial tension $\sigma$ due to curvature $R_c$,
gives pressure $P_s = \sigma/R_c$,

For typical values $P_s >> P_g$

# PR Planarization #2



$$H(t) = H_0 / [\ 1 + (\ 16P_s /3R^2\mu\ )\ H_0^2 t\ ]^{1/2}$$

For typical values

$H \rightarrow H_0/2$ for $t \sim 10^{-4}$s

Small features almost totally planarized out.

Carbon: group IV, 4 electrons/atom:

- 2 paired with adjacent covalent carbons
- 1 paired with adjacent hydrogen
- 1 → delocalized ring

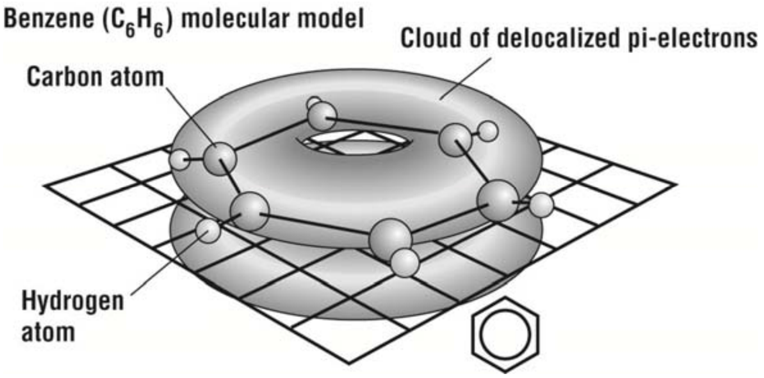


**Figure 8.1** Diagram of simple benzene aromatic ring. The delocalized pi-bond electrons are in a ring that surrounds the nuclei. The symbol indicates the currently accepted ring notation.

## H substitutions

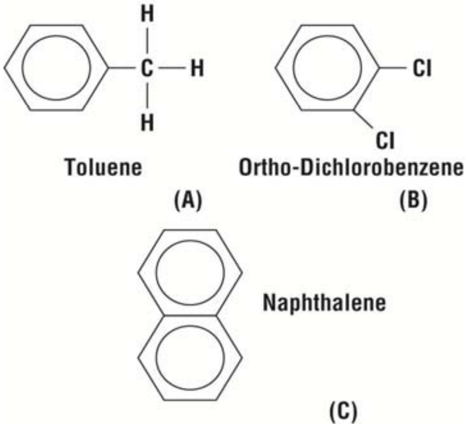
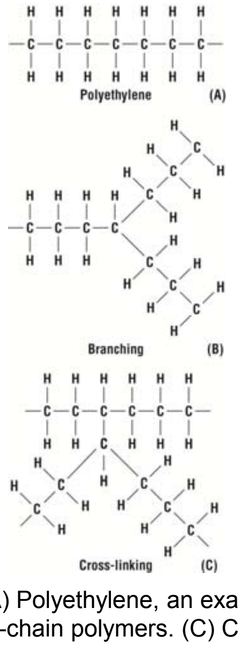


**Figure 8.2** Some aromatic-based compounds based on (A) single-site substitution, (B) double-site substitution, where the first term defines the position (ortho, meta, or para) of the second substitution relative to the first, and (C) aromatic condensation.

Note: − indicates 1 electron from each atom, e.g. C – H
= indicates 2 electrons from each atom, e.g. C = H

Simplest polymer

$CH_2$ monomer



Positive PR:
Exposure → chain scission
(Dissolves more readily in developer)

Negative PR:
Exposure → chain cross-linking
(Dissolves less readily in developer)

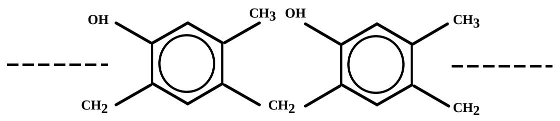
**Figure 8.3** (A) Polyethylene, an example of a simple polymer.
(B) Branched-chain polymers. (C) Cross-linking.

## Photoresists

- Resists are organic polymers that are spun onto wafers and prebaked to produc a film ≈ 0.5 - 1 μm thick.

## g-Line and i-Line Resists

- Generally consist of 3 components:
  - Inactive resin
  - Photoactive compound (PAC)
  - Solvent - used to adjust viscosity
- After spinning and baking resists ≈ 1:1 PAC and resin.
- Diazonaphthoquinone or DNQ resists are commonly used today for g-line and i-line resists.



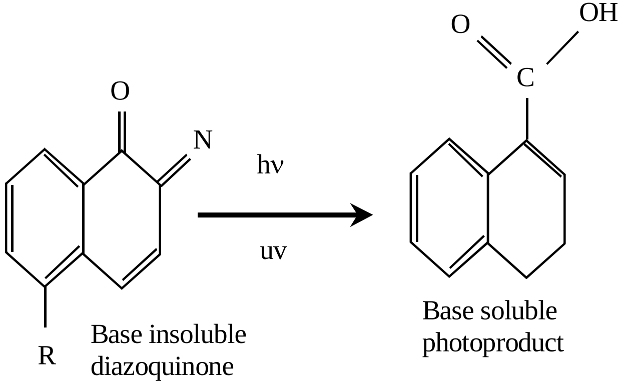
- The base resin is novolac a long chain polymer consisting of hydrocarbon rings with 2 methyl groups and 1 OH group attached.

- g and i-line resists based on DNQ materials were used down to 0.35 μm.

- DUV resists use chemical amplification and are generally used below 0.35 μm.

# Positive UV PR Chemistry

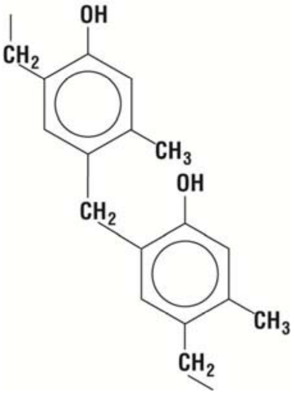
- A 2-component positive resist: DQN



In phenol-formaldehyde copolymer matrix (novolak)

## DQN

(for i-line and g-line)



"-N"
Novolac matrix
(adhesive)

**Figure 8.4** Meta-Cresol novolac, a commonly used resin material in g- and i-line applications. The basic ring structure may be repeated from 5 to 200 times.

## DQN

Positive PR

DQ-
diazoquinone

Photo-active compound
(PAC)

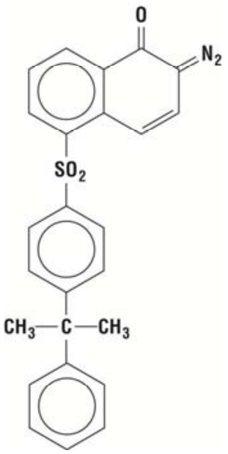
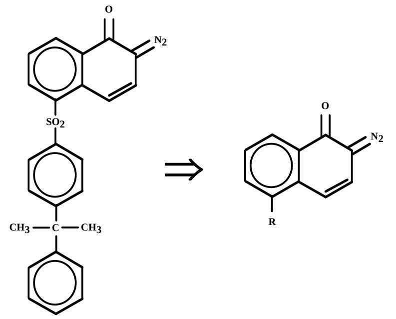
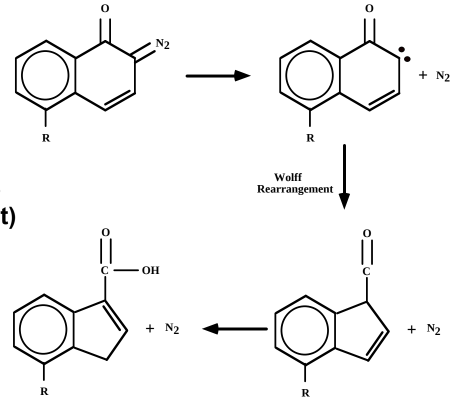


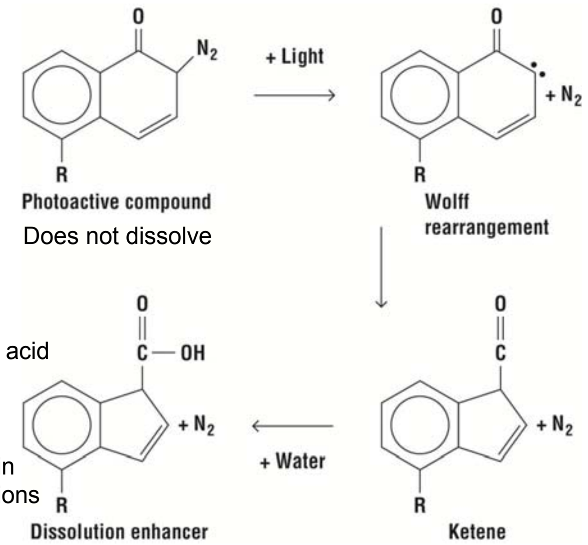
**Figure 8.5** Diazo quinone (DQ), the most commonly used photoactive compound for g- and i-line applications. The right-hand ring is not an aromatic but has a double bond.



- The PACs in DNQ resists are often diazoquinones. The photoactive portion is above the $SO_2$.
- Diazoquinones are insoluble in typical developers and reduce the dissolution rate of unexposed resists to ≈ 1 - 2 nm $sec^{-1}$.



- After exposure to light, the PAC component in DNQ resists undergoes a transformation (Wolff rearrangement) into carboxylic acid which is soluble in the developer (basic solution).



Frees $N_2$ + reactive ring

Does not dissolve

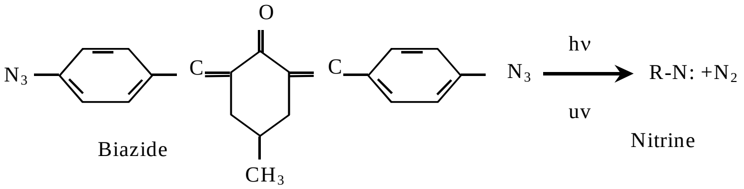
Carboxylic acid

Dissolves in base solutions pH>7

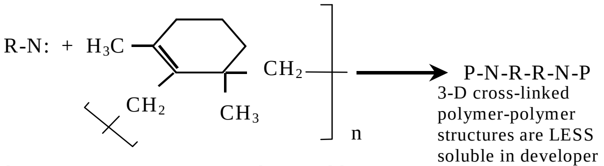
**Figure 8.6** Photolysis and subsequent reactions of DQ upon UV exposure.

Typical developers: aqueous KOH, NaOH solutions

# Negative UV PR Chemistry



- A 2-component negative resist



Poly cis-isoprene matrix (synthetic rubber)

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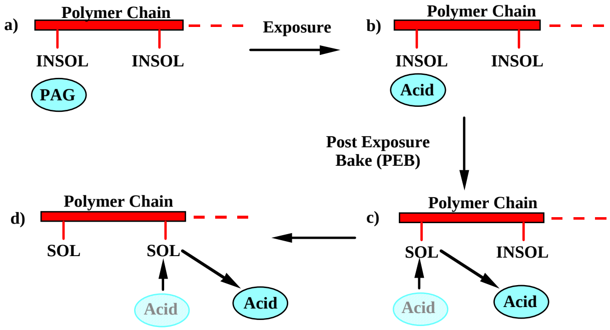
## DUV (Deep Ultraviolet) Resists

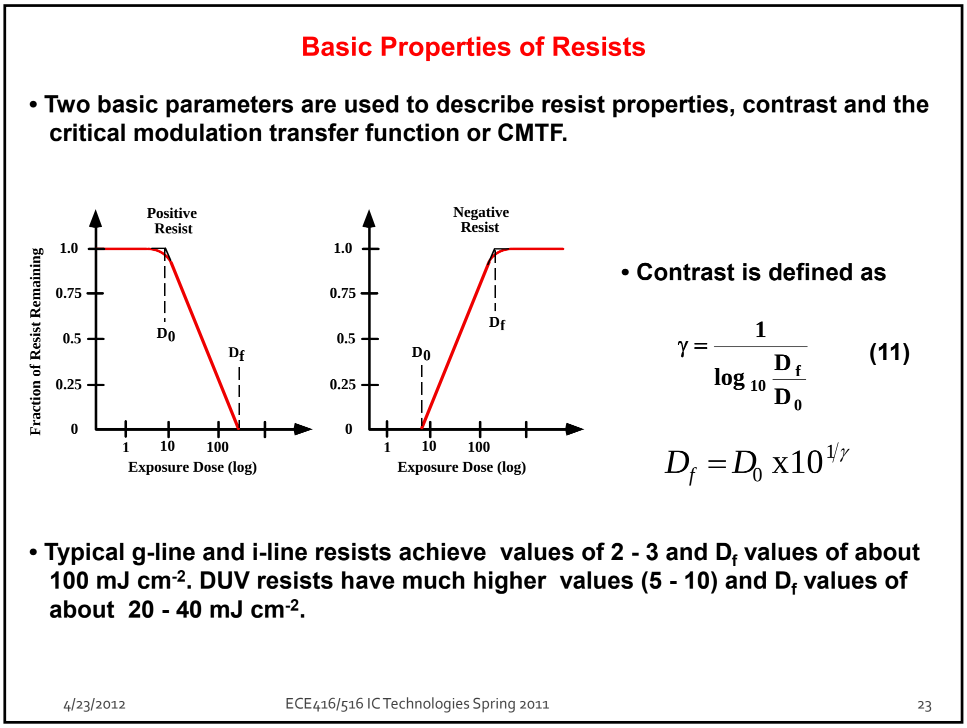
- **g-line and i-line resists have maximum quantum efficiencies < 1 and are typically ≈ 0.3.**
- **Chemical amplification (CA) can improve this substantially.**
- **DUV resists all use this principle. A catalyst is used.**
- **Photo-acid generator (PAG) is converted to an acid by photon exposure. Later, in a post exposure bake, the acid molecule reacts with a “blocking” molecule on a polymer chain, making it soluble in developer AND REGENERATING THE ACID MOLECULE**

**∴ catalytic action ∴ sensitivity is enhanced.**



← Catalytic action

Both positive and negative PRs



## Basic Properties of Resists

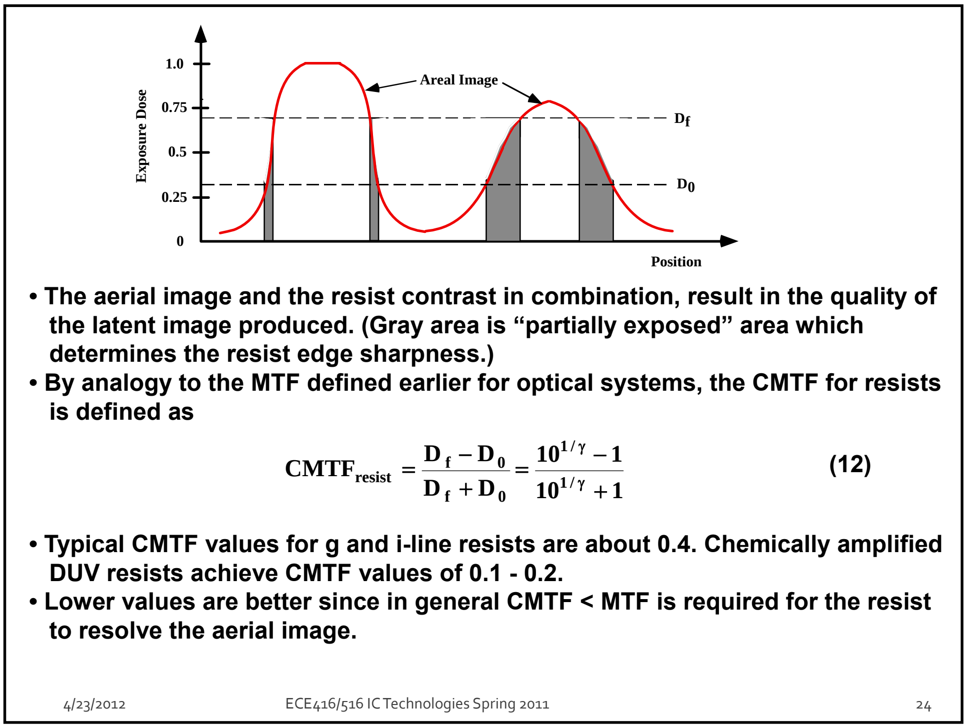
- Two basic parameters are used to describe resist properties, contrast and the critical modulation transfer function or CMTF.

- Contrast is defined as

$$\gamma = \frac{1}{\log_{10} \frac{D_f}{D_0}} \qquad (11)$$

$$D_f = D_0 \, x10^{1/\gamma}$$

- Typical g-line and i-line resists achieve  values of 2 - 3 and $D_f$ values of about 100 mJ $cm^{-2}$. DUV resists have much higher  values (5 - 10) and $D_f$ values of about  20 - 40 mJ $cm^{-2}$.

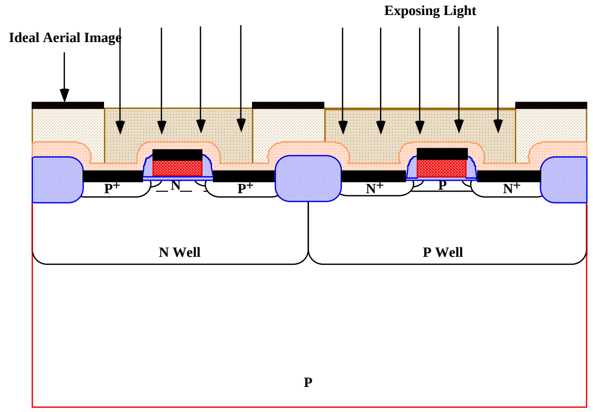


- The aerial image and the resist contrast in combination, result in the quality of the latent image produced. (Gray area is “partially exposed” area which determines the resist edge sharpness.)
- By analogy to the MTF defined earlier for optical systems, the CMTF for resists is defined as

$$\mathrm{CMTF}_{\mathrm{resist}} = \frac{D_f - D_0}{D_f + D_0} = \frac{10^{1/\gamma} - 1}{10^{1/\gamma} + 1} \qquad (12)$$

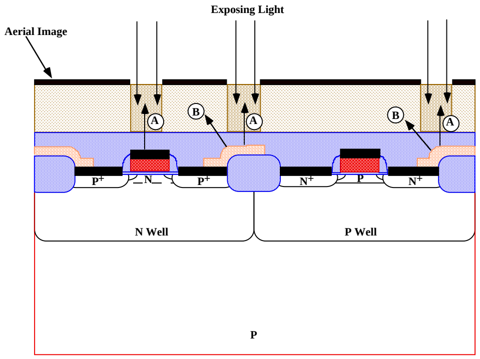
- Typical CMTF values for g and i-line resists are about 0.4. Chemically amplified DUV resists achieve CMTF values of 0.1 - 0.2.
- Lower values are better since in general CMTF < MTF is required for the resist to resolve the aerial image.

- There are often a number of additional issues that arise in exposing resist.

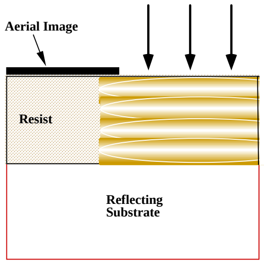


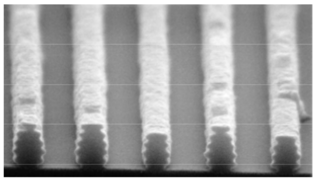
- Resist is applied as a liquid and hence "flows" to fill in the topography.

∴ Resist thickness may vary across the wafer. This can lead to under or over exposure in some regions and hence linewidth variations.



- Reflective surfaces below the resist can set up reflections and standing waves and degrade resolution.
- In some cases an antireflective coating (ARC) can help to minimize these effects. Baking the resist after exposure, but before development can also help.





(Photo courtesy of A. Vladar and P. Rissman, Hewlett Packard.)

$D_f \rightarrow D_{100}$ in Campbell

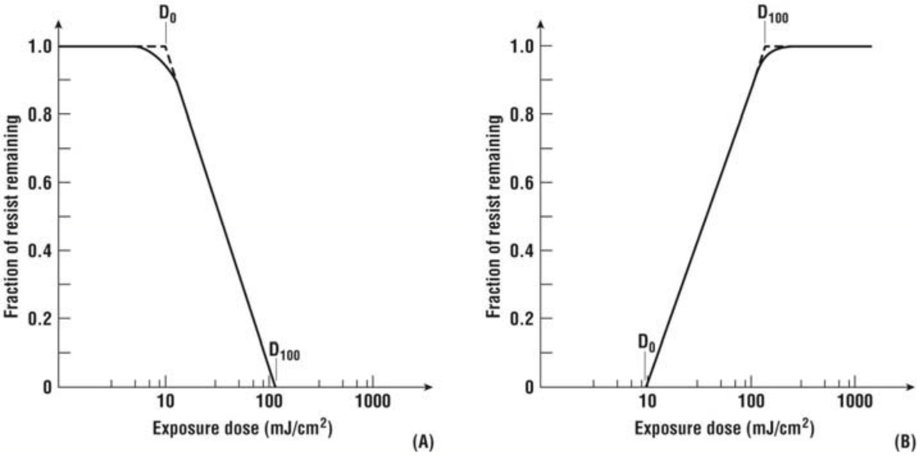
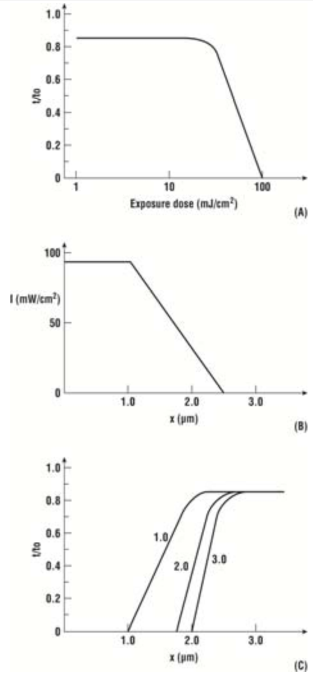


**Figure 8.7** Contrast curves for idealized resists: (A) postitive tone and (B) negative tone.

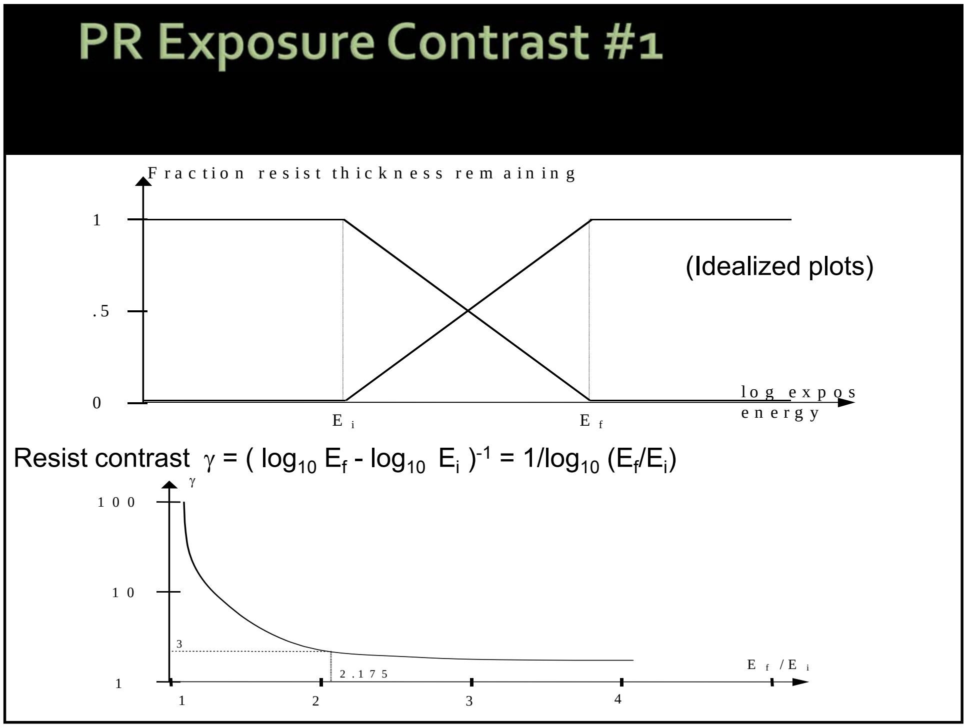


Example 8.2

Positive PR contrast curve (thickness/original thickness) (y-axis)

Areal image x time → dose (x-axis)

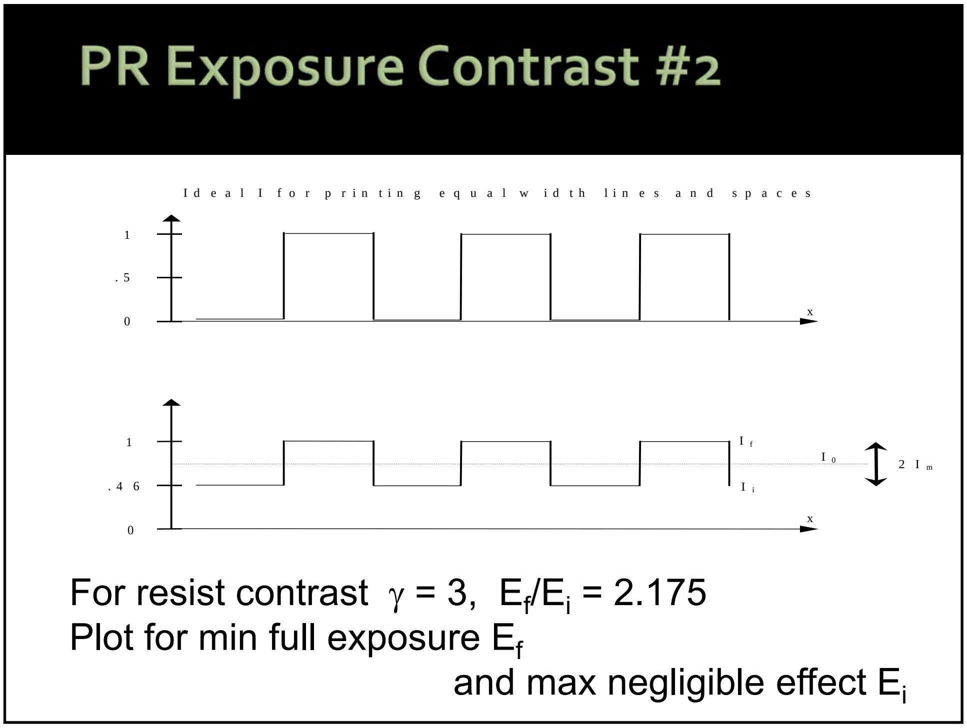
**Figure 8.8** (A) Measured contrast curve for a commercial DQN resist. (B) Simple areal image. (C) Approximate profiles for 1-, 2-, and 3-sec exposures.



# PR Exposure Contrast #1

(Idealized plots)

Resist contrast $\gamma = (\log_{10} E_f - \log_{10} E_i)^{-1} = 1/\log_{10} (E_f/E_i)$



# PR Exposure Contrast #2

For resist contrast $\gamma = 3$, $E_f/E_i = 2.175$

Plot for min full exposure $E_f$

and max negligible effect $E_i$

# PR Exposure Contrast #3

Need wave modulation of image $M_i = I_m/I_0$

For lines to just print , $I_i = I_0 - I_m$, $I_f = I_0 + I_m$

ie. critical modulation for acceptable print

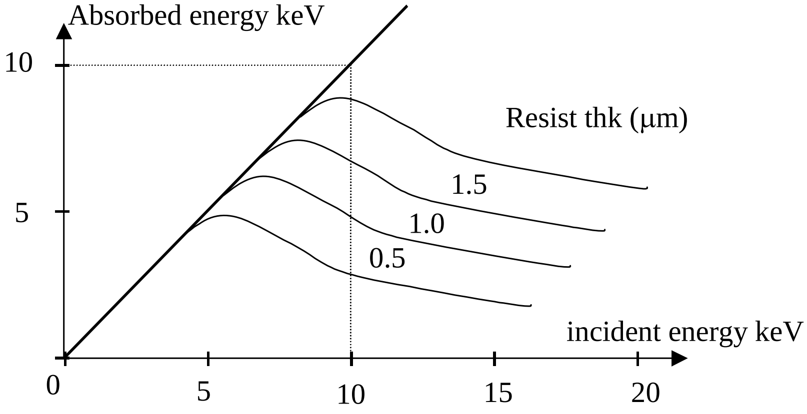
$$M_{ic} = (I_f - I_i) / (I_f + I_i)$$
$$= (10^{1/\gamma} - 1) / (10^{1/\gamma} + 1)$$

For mask source modulation $M_s = 1$ ,

$M_{ic}$ represents optics quality.

If $\gamma$ increases, can print with lower $M_i$

# PR Exposure Physics #1



Low energy --> all absorbed

High energy --> photon/electron goes straight through

# PR Exposure Physics #2

Total number scissions $N^*$ from dose D:

$N^* = K\,D\,w$

where w polymer mass, K a molecular parameter

Av molecular weight $M_n^o = w\,N_a / N_0$

$N_0$ number molecules in mass w

$N_a$ Avogadro's number

After exposure $M_n \rightarrow w\,N_a / (N_0 + N^*)$

$\therefore M_n^{-1} = M_n^{o-1} + (K/N_a)D$

Want high k for feature definition

# Energy absorption in PR

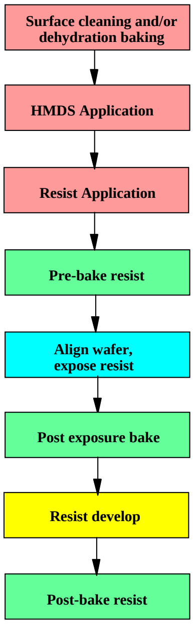
Given $I(z) = I_0 e^{-\alpha z}$

Energy absorption in PR of thickness $T_R$ :

$$A = \frac{\int_0^{T_R} \left[ I_0 - I(z) \right] dz}{I_0 T_R} = \frac{I_0 (T_R - 0) - (-1/\alpha)(e^{-\alpha T_R} - e^{-0})}{I_0 T_R}$$

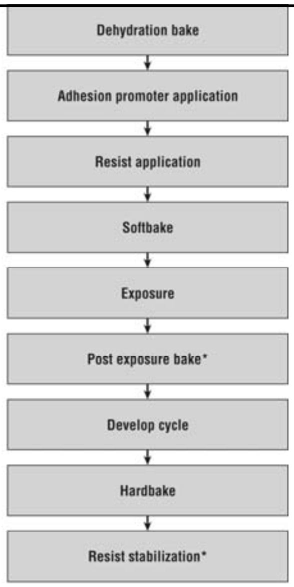
$$= 1 - \frac{1 - e^{-\alpha T_R}}{\alpha T_R}$$

## Typical resist process:



| | | |
|---|---|---|
| Surface cleaning and/or dehydration baking | Prepares surface for photoresist application | |
| HMDS Application | Adhesion promoter typically spun on the wafer | |
| Resist Application | Resist spun on wafer, typically 3000-6000 rpm, forming an - 0.5 µm resist layer | |
| Pre-bake resist | Typically 10 - 30 min @ 90 - 100 ÞC | |
| Align wafer, expose resist | Typically aligned at each exposure site, exposed at 150 mJ $cm^{-2}$ | **(Smaller dose for DUV resists)** |
| Post exposure bake | Sometimes used to minimize standing waves in resist Typically 10 min @ 100ÞC | **(Required for DUV resists)** |
| Resist develop | Typically 30 - 60 sec @ room T using spray or immersion | |
| Post-bake resist | Typically 10 - 30 min @ 100 - 140 ÞC | |

**(g and i-line resist parameters)**



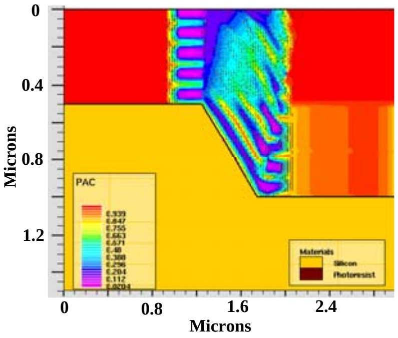
← PR thickness:
$TR\ \alpha\ 1/\sqrt{\omega}$ where ω is spin speed

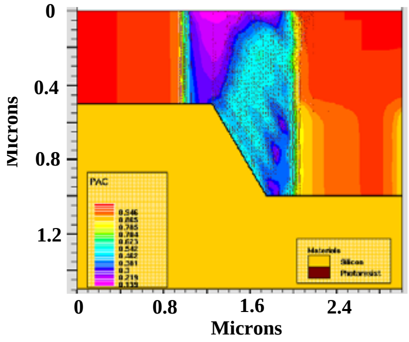
*Optional steps

**Figure 8.9** Typical process flow in a photolithography step.

## D. Photoresist Baking

- A post exposure bake is sometimes used prior to developing the resist pattern.
- This allows limited diffusion of the exposed PAC and smoothes out standing wave patterns.
- Generally this is modeled as a simple diffusion process.





- Simulation on right after a post exposure bake of 45 minutes at 115 ˚C. The color contours again correspond to the [PAC] after exposure. Note that the standing wave effects apparent earlier have been “smeared out” by this bake, producing a more uniform [PAC] distribution.

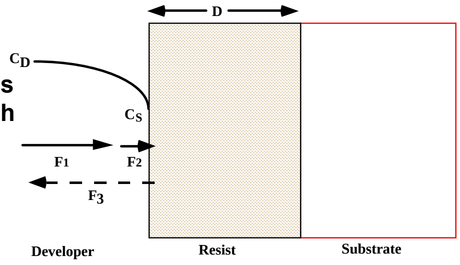
## E. Photoresist Developing

- A number of models for resist developing have been proposed and implemented in lithography simulators.
- The simplest is purely empirical (Dill et.al).

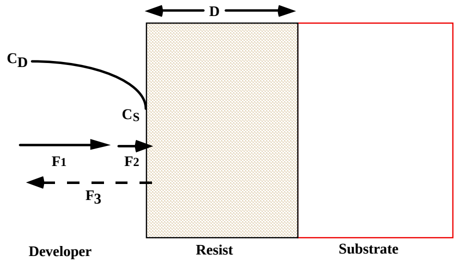
$$R(x,y,z)=\begin{cases} 0.006\exp\left(E_1+E_2m+E_3m^2\right) & \text{if}\quad m>-0.5\dfrac{E_2}{E_3} \\ 0.006\exp\left(E_1+\dfrac{E_2}{E_3}(E_2-1)\right) & \text{otherwise} \end{cases} \qquad (28)$$

where R is the local developing rate and m is the local [PAC] after exposure. $E_1$, $E_2$ and $E_3$ are empirical constants.

- A more physically based model has been developed by Mack which models developer diffusion and reaction (much like deposition models).
- See next slide for details on this development model.



# Mack PR development model I



$F_1 = k_D(C_D - C_S)$

where $k_D$ = mass transfer coefficient (for developer diffusion)

$C_D$ = bulk developer concentration

$C_S$ = surface developer concentration

and $F_2 = k_R C_S [P]^n$

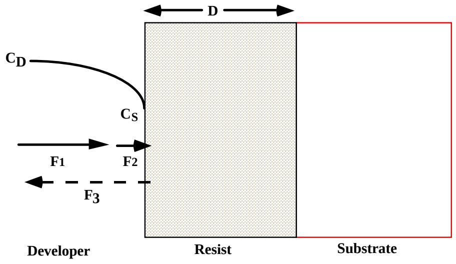
where $k_R$ = developer-resist reaction rate constant

$[\mathrm{P}]$ = local concentration of P (reacted PAC) $= [\mathrm{PAC}]_0 - [PAC]$ and $m = [PAC]/[PAC]_0$

and $n$ = molecules of P react with developer to dissolve one PR resin molecule

Development rate $r = F_1 = F_2 = \dfrac{k_D k_R C_D [P]^n}{k_D + k_R [P]^n} = \dfrac{k_D C_D (1-m)^n}{\dfrac{k_D}{k_R [PAC]_0^n} + (1-m)^n}$

# Mack PR development model II



$$r = F_1 = F_2 = \frac{k_D k_R C_D [P]^n}{k_D + k_R [P]^n} = \frac{k_D C_D (1-m)^n}{\dfrac{k_D}{k_R [PAC]_0^n} + (1-m)^n}$$

→ 0 for $m = 1$ (unexposed resist) so modify to

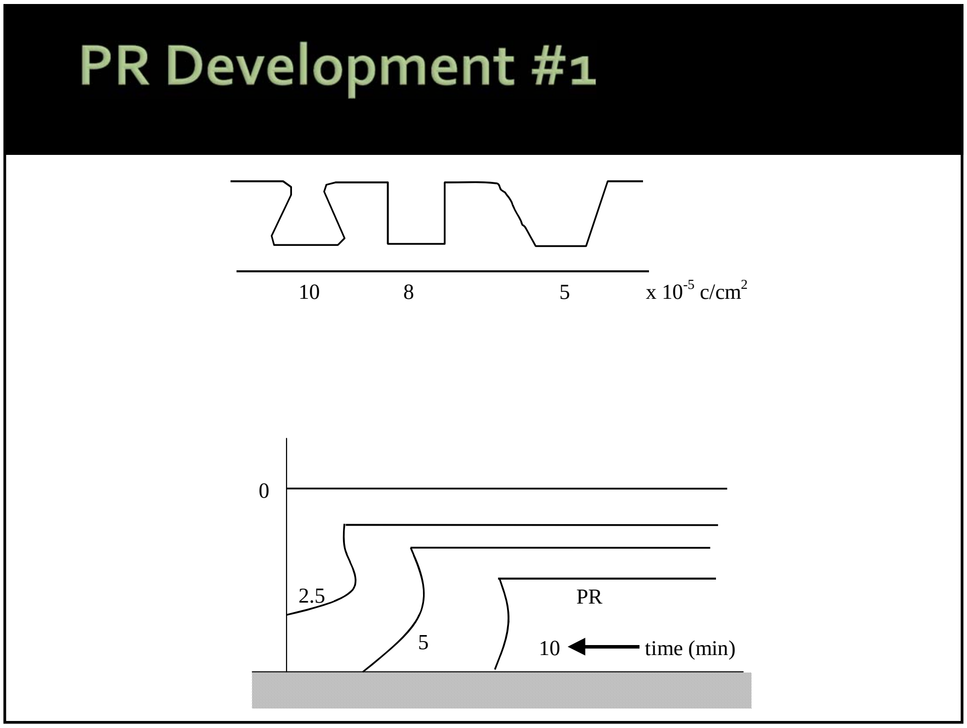
$$r = \frac{k_D C_D (1-m)^n}{\dfrac{k_D}{k_R [PAC]_0^n} + (1-m)^n} + r_{\min}$$

$$\to r_{\max} = \frac{k_D C_D}{\dfrac{k_D}{k_R [PAC]_0^n} + 1} + r_{\min} \text{ for } m = 0 \text{ (PR fully exposed)}$$

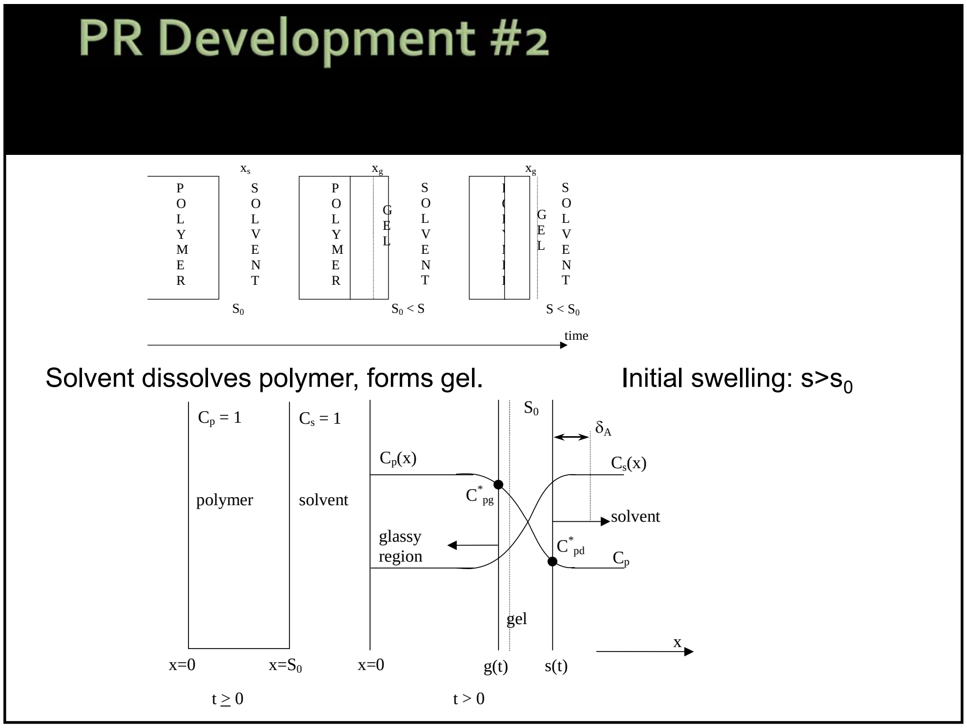
$$\text{so } r = r_{\max} \frac{(a+1)(1-m)^n}{a + (1-m)^n} \text{ where } a = \frac{k_D}{k_R [PAC]_0^n}$$

Surface reaction rate limited: $r \approx k_R C_D [P]^n + r_{\min}$

Diffusion rate limited: $r \approx k_D C_D + r_{\min}$



# PR Development #1



# PR Development #2

Solvent dissolves polymer, forms gel.

Initial swelling: $s>s_0$

# PR Development #3

Volume fractions polymer & solvent

$C_p + C_s = 1$

$\partial c / \partial t = \partial ( D_s \partial C_s / \partial x ) / \partial x$

$D_s$ = diffusion coefficient of solvent in polymer

Initial condition $C_s = 0,\ 0 < x < s_0 \quad t \leq 0$
At $x = 0,\ \partial C_s / \partial x = 0$
At $x = s(t),\ D_s(\partial C_s/\partial x) - k_{dC}\, C_{pd}^* = ds/dt$
At $x= g(t),\ C_s\, dy/dt = -D_s\, \partial C_s / \partial x$
& $C_s = C_{sg}^*$ or $C_p = 1 - C_{sg}^* = C_{pg}^*$

# PR Development #4

Assume linear concentration approximation in gel

At x=g(t),

$(1-C_{pg}^*)dy/dt = D_s(C_{pd}^*-C_{pg}^*)/(s(t) - g(t))$

At x=s(t),

$ds/d = D_s(C_{pg}^* - C_{pd}^*) / (s(t) - g(t)) - k_d\, c_{pd}^*$

giving

$d(s-g)/dt=D_s(C_{pg}^*-C_{pd}^*)(2-C_{pg}^*)/(1-C_{pg}^*)(s-g)-k_d c_{pd}^*$

$(s - g) = 0$ at $t = 0$

# PR Development #5

Solution is

$$-A\delta - AB\ln(1 - \delta/B) = \tau$$

where $\delta = (s - g)/s_0$

$$A = D_s / s_0 k_d C_{pd}^*$$

$$B = D_s(C_{pg}^* - C_{pd}^*)(2 - C_{pg}^*) / s_0 k_d C_{pd}^*(1 - C_{pg}^*)$$

$$\tau = D_s t / s_0^2$$

For small t, $\delta = (2B\,\tau/A)^{1/2}$

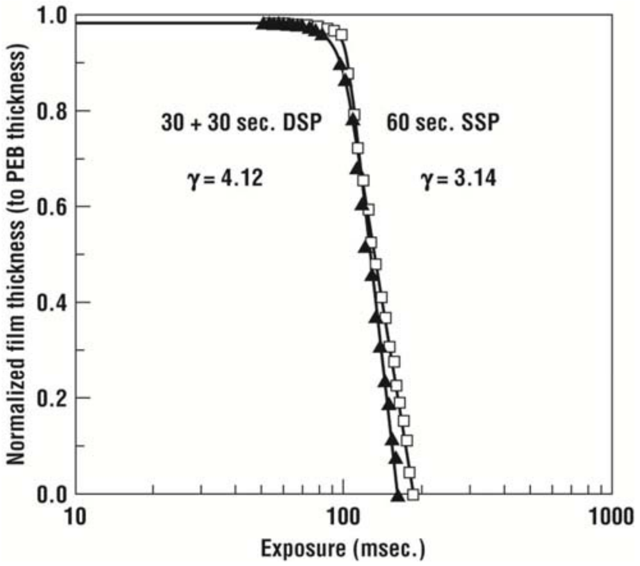
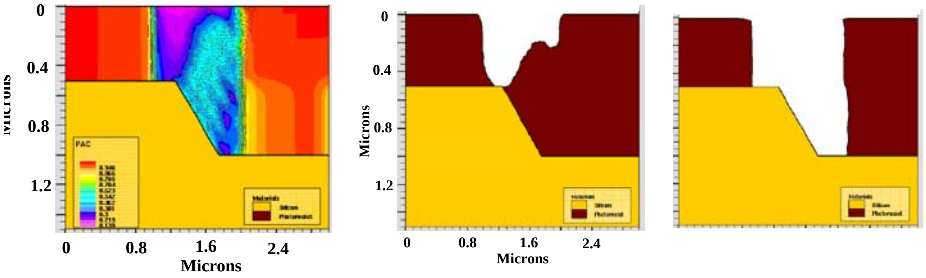
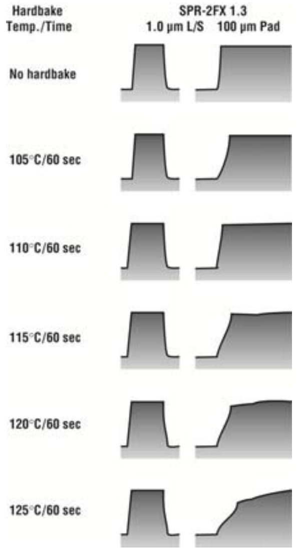


**Figure 8.10** Contrast curves for Megaposit SPR500 resist using MF CD-26 developer *(courtesy Shipley).*

D/SSP: double/single spray puddle (dispense)



- **Example of the calculation of a developed photoresist layer using the ATHENA simulator. The resist was exposed with a dose of 200 mJ $cm^{-2}$, a post exposure bake of 45 min at 115 ˚C was used and the pattern was developed for a time of 60 seconds, all normal parameters. The Dill development model was used. Center - part way through development. Right - complete development.**



Hardness against future
processing, e.g. etch,
ion implantation
(shallow profile useful?)

**Figure 8.11** Resist profiles of a 1-µm line and space and a large feature in SPR-2FX resist for different hardbake temperatures *(courtesy Shipley).*

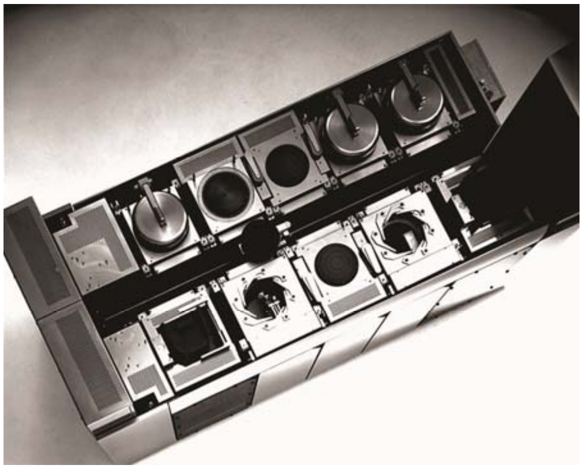


**Figure 8.12** Top view of a photoresist processing system including cassette load and unload, resist application, bake and develop stations, and a central robot; more modern systems are in a controlled environment and integrated into an exposure tool *(courtesy silicon Valley Group)*.

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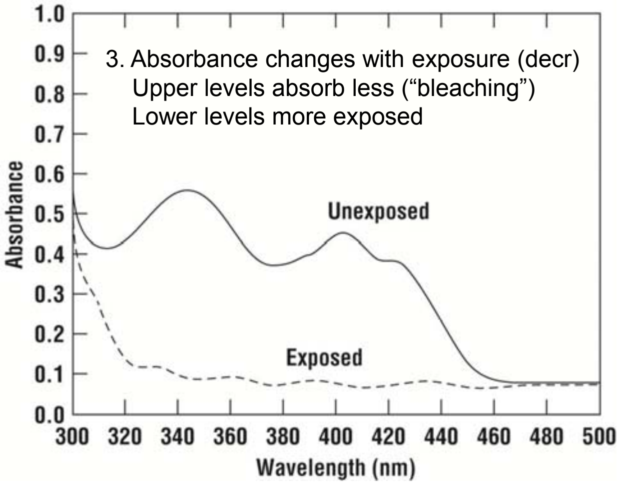
## Second order effects

1. Large PR α→ energy absorbed at top, bottom under develops
2. Light absorbed by resin/matrix does not reach PAC. (Novolac absorbs DUV)



3. Absorbance changes with exposure (decr)
   Upper levels absorb less ("bleaching")
   Lower levels more exposed

**Figure 8.13** Total absorbance of a layer of SPR511-A resist before and after exposure. The difference between the two curves is the actinic absorbance *(courtesy Shipley).*

Example 8.5 Simulation

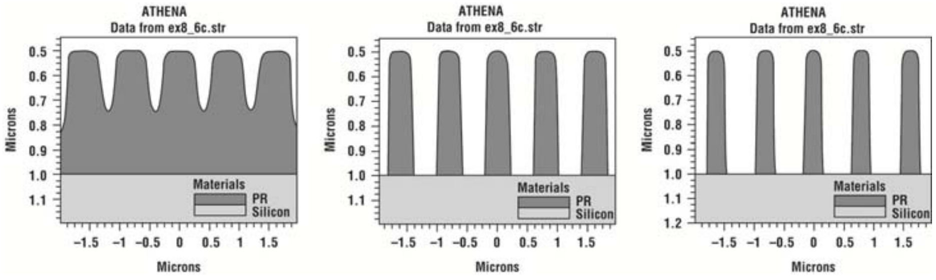


**Figure 8.15** Resist profiles for 60, 100, and 140 mJ/cm2. Notice the line narrowing (W < 0.4 μm) at the higher dose. Dose optimization will require a measurement of the line width as a function of the dose (swing curve).

Future
e.g. inorganic PR –
polarity changes in the molecule

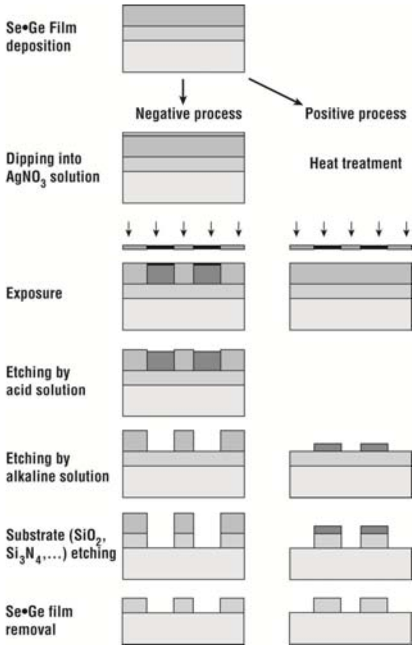
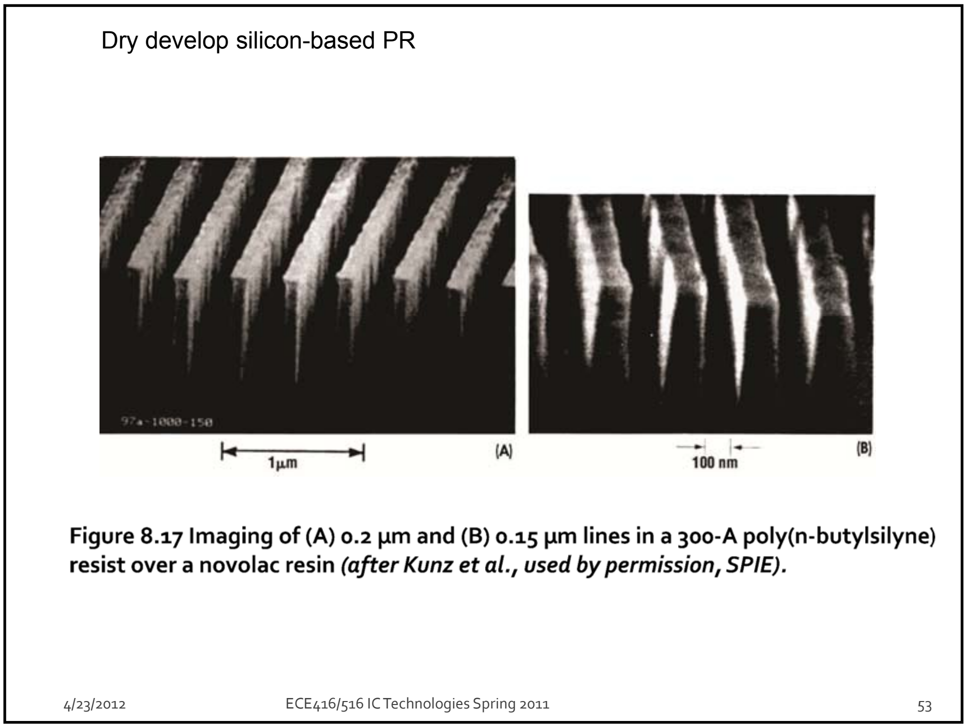


**Figure 8.16** Processing sequence for Ag/Se–Ge resists *(after Yoshikawa et al., reprinted by permission, AIP).*



Dry develop silicon-based PR

**Figure 8.17 Imaging of (A) 0.2 μm and (B) 0.15 μm lines in a 300-A poly(n-butylsilyne) resist over a novolac resin *(after Kunz et al., used by permission, SPIE).***