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

Patterned resist

Negative resist
Dissolve not exposed

Positive resist
Dissolve exposed

UV light
**Photoresist Exposure**

Positive PR MORE soluble in developer after exposure 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

\[ \therefore \text{ Navier-Stokes equation} \]

\[ \mu \left( \frac{\partial^2 v_r}{\partial z^2} \right) = -\rho \omega^2 r , \]

where \( \mu, \rho \) = liquid viscosity, density

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

where \( q = \int_0^h v_r \, dz \) = volumetric flow rate

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**PR Spin Coating #2**

Boundary Conditions:
- No slip at wafer surface, \( v_r = 0 \) at \( z = 0 \)
- No shear stress at free surface,

\[ \frac{dv_r}{dz} = 0 \] at \( z=h(r, t) \)

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

& \quad q = \left( \rho \omega^2 r/3\mu \right) h^3(t)

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

Solution for \( h = h_0 \) at \( t = 0 \):

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

ie. uniform thickness if initially uniform

Also for \( h << h_0 \) (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

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Planarization

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 $P_s \gg P_g$
PR Planarization #2

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

For typical values

\[ H \rightarrow \frac{H_0}{2} \text{ for } t \sim 10^{-4}s \]

Small features almost totally planarized out.

Carbon: group IV, 4 electrons/atom:

2 paired with adjacent covalent carbons
1 paired with adjacent hydrogen
1 \rightarrow 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.
**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

**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 produce 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.

\[
\text{CH}_2 \text{CH}_3 \text{CH}_3 \text{CH}_2 \text{CH}_2 \text{OH} \text{OH}
\]

- 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.

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Positive UV PR Chemistry

- **A 2-component positive resist: DQN**

\[
\text{O} \quad \text{O} \\
\text{N} \quad \text{C} \\
\text{R} \quad \text{OH}
\]

In phenol-formaldehyde copolymer matrix (novolak)
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.

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 SO₂.

• Diazooquinones 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).
Negative UV PR Chemistry

- A 2-component negative resist

![Chemical structure diagram]

Poly cis-isoprene matrix (synthetic rubber)

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.

![Chemical reaction diagram]
**Basic Properties of Resists**

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

\[
\gamma = \frac{1}{\log_{10} \left( \frac{D_f}{D_0} \right)}
\]  

(11)

- Contrast is defined as

\[
D_f = D_0 \times 10^\frac{1}{\gamma}
\]

- Typical g-line and i-line resists achieve values of 2 - 3 and Dᵢ values of about 100 mJ cm⁻². DUV resists have much higher values (5 - 10) and Dᵢ 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

\[
\text{CMTF}_{\text{resist}} = \frac{D_f - D_0}{D_f + D_0} = \frac{10^{1/\gamma} - 1}{10^{1/\gamma} + 1}
\]  

(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.)
Figure 8.7  Contrast curves for idealized resists: (A) positive 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 DON resist. (B) Simple areal image. (C) Approximate profiles for 1-, 2-, and 3-sec exposures.
Resist contrast \( \gamma = (\log_{10} E_f - \log_{10} E_i)^{-1} = \frac{1}{\log_{10} (E_f/E_i)} \)

For resist contrast \( \gamma = 3 \), \( E_f/E_i = 2.175 \)
Plot for min full exposure \( E_f \) and max negligible effect \( E_i \)
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

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

For mask source modulation $M_s = 1$, $M_{ic}$ represents optics quality.

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

Low energy --> all absorbed

High energy --> photon/electron goes straight through
Total number scissions $N^*$ from dose $D$:

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

where $w$ polymer mass, $K$ a molecular parameter

Av molecular weight $M_n^0 = w \, N_a / N_0$

$N_0$ number molecules in mass $w$

$N_a$ Avogadro’s number

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

$$M_n^{-1} = M_n^0 + (K/N_a)D$$

Want high $k$ for feature definition

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**Energy absorption in PR**

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

Energy absorption in PR of thickness $T_R$:

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

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

Align wafer, expose resist
Typically aligned at each exposure site, exposed at 150 mJ cm⁻²

Post exposure bake
Sometimes used to minimize standing waves in resist
Typically 10 min @ 100 °C

Resist develop
Typically 30 - 60 sec @ room T using spray or immersion

Post-bake resist
Typically 10 - 30 min @ 100 - 140 °C

Figure 8.9 Typical process flow in a photolithography step.

Dehydration bake
Adhesion promoter application
Resist application
Softbake
Exposure
Post-exposure bake
Develop cycle
Hardbake
Resist stabilization

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

*Optional steps
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).

\[
R(x, y, z) = \begin{cases} 
0.006e^{E_1 + E_2m + E_3m^2} & \text{if } m > -0.5 \frac{E_2}{E_3} \\
0.006e^{E_1 + \frac{E_2}{E_3}(E_2 - 1)} & \text{otherwise} 
\end{cases} 
\]  

(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 \( F_2 = k_s C_s[P] \)
where \( k_s \) = developer - resist reaction rate constant
\( [P] \) = local concentration of P (reacted PAC) = \([PAC]_b - [PAC]\) \( m = [PAC] / [PAC]_b \)
and \( n \) = molecules of P react with developer to dissolve one PR resin molecule

Development rate \( r = r_1 = r_2 = k_s k_o C_s[P] \)
\[ r = \frac{k_s C_s(1-m)^y}{k_D + k_s[P]} = \frac{k_s C_s(1-m)^y}{k_D k_s[PAC]_b + (1-m)^y} + r_{\text{diff}} \]

\( r_{\text{diff}} \) = limited rate diffusion
\( r_{\text{surf}} \) = limited rate reaction surface

\( r = 0 \) for \( m = 1 \) (unexposed resist) so modify to
\( r = \frac{k_s C_s(1-m)^y}{k_s[PAC]_b + (1-m)^y} + r_{\text{surf}} \)

so \( r_{\text{surf}} = (a + 1)(1-m)^y \)
where \( a = \frac{k_o}{k_s[PAC]_b} \)

Mack PR development model II

\[ r = F_1 = F_2 = k_s k_o C_s[P] \]
\[ r = \frac{k_s C_s(1-m)^y}{k_D + k_s[P]} = \frac{k_s C_s(1-m)^y}{k_D k_s[PAC]_b + (1-m)^y} + r_{\text{diff}} \]

\( r_{\text{diff}} \) = limited rate diffusion
\( r_{\text{surf}} \) = limited rate reaction surface

\( r = 0 \) for \( m = 1 \) (unexposed resist) so modify to
\( r = \frac{k_s C_s(1-m)^y}{k_s[PAC]_b + (1-m)^y} + r_{\text{surf}} \)

\( r_{\text{surf}} = (a + 1)(1-m)^y \)
where \( a = \frac{k_o}{k_s[PAC]_b} \)

Surface reaction rate limited : 
\( r = k_s C_s[P] + r_{\text{surf}} \)
Diffusion rate limited : 
\( r = k_s C_s + r_{\text{surf}} \)
PR Development #1

After development, e.g. for electron doses $10^8 \times 10^{-5} \text{ c/cm}^2$

Solvent dissolves polymer, forms gel. Initial swelling: $s > s_0$

$P \rightarrow L \rightarrow Y \rightarrow M \rightarrow E \rightarrow R$

Solvent dissolves polymer, forms gel.

Initial swelling: $s > s_0$

$C_p = 1$
$C_s = 1$

$C_p(x)$
$C_s(x)$

$g(t)$ $s(t)$

Initial swelling: $s > s_0$

$C_{pol}$
$C_{gel}$

Solvent region

glassy region
Volume fractions polymer \& solvent
\[ C_p + C_s = 1 \]
\[ \frac{\partial c}{\partial t} = \frac{\partial}{\partial x} \left( D_s \frac{\partial C_s}{\partial x} \right) \]
\[ D_s = \text{diffusion coefficient of solvent in polymer} \]

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

Assume linear concentration approximation in gel
At \( x = g(t) \),
\[ (1-C_{pg}^*) \frac{dy}{dt} = D_s (C_{pd}^* - C_{pg}^*) / (s(t) - g(t)) \]
At \( x = s(t) \),
\[ \frac{ds}{dt} = D_s (C_{pg}^* - C_{pd}^*) / (s(t) - g(t)) - k_d C_{pd}^* \]
giving
\[ \frac{d(s-g)}{dt} = D_s (C_{pg}^* - C_{pd}^*) (2-C_{pg}^*) / (1-C_{pg}^*) (s-g) - k_d C_{pd}^* \]
\[ (s - g) = 0 \text{ at } t = 0 \]
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 \(t\), \(\delta = (2B \tau/A)^{1/2}\)
• 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.

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).

Second order effects
1. Large PR $\alpha \rightarrow$ 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).
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).

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).