Lecture 50
Lithography:
Photoresist ABCs

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Exposure Kinetics
• Photoresist exposure is first-order

\[
\frac{dM}{dt} = -CI \frac{M}{t}
\]

where
- \( M \) = Sensitizer Concentration
- \( I \) = Light Intensity
- \( t \) = Exposure Time
- \( C \) = Exposure Rate Constant
- \( t \) = Exposure Dose (energy)

• If \( I \) is constant with time,

\[
m = \frac{M}{M_0} = e^{-Ct}
\]

\( M_0 \) = Initial (unexposed) sensitizer concentration

Lambert Law of Absorption
• This is a well established empirical law:

\[
\frac{dI}{dz} = -\alpha I
\]

where
- \( I \) = Light intensity
- \( z \) = Depth into the absorbing material
- \( \alpha \) = Absorption coefficient

Note: \( \alpha < \frac{4\pi \kappa}{\lambda} \) where \( \kappa \) = imaginary part of refractive index

Beer’s Law
• This is an empirical law with many exceptions:

\[
\alpha = a_i c_i
\]

where
- \( a_i \) = molar absorptivity of material \( i \)
- \( c_i \) = concentration of material \( i \)

• For a multicomponent material,

\[
\alpha = \sum a_i c_i
\]

Beer’s Law
• For a standard positive photoresist,

\[
\alpha = a_M M + a_P P + a_R R + a_S S + \ldots
\]

where
- \( M \) = Sensitizer concentration
- \( P \) = Exposed sensitizer concentration
- \( R \) = Resin concentration
- \( S \) = Solvent concentration

Absorption Coefficient
• Grouping exposure-dependent terms,

\[
\alpha = Am + B
\]

\[
A = (a_M - a_P)M_0 + a_R M_0 + a_R R + a_S S
\]

\( A \) = bleachable absorption coefficient
\( B \) = non-bleachable absorption coefficient
\( m \) = relative sensitizer concentration
Absorption (non-reflecting substrate)

- Exposure Kinetics
  \[ \frac{\partial m}{\partial t} = -C I m \]

- Absorption (non-reflecting substrate)
  \[ \frac{\partial I}{\partial z} = -(A m + B I) \]

ABC Parameters (also called Dill parameters)

Measuring the Dill ABC Parameters

\[ A = \frac{1}{D} \ln \left( \frac{T(\infty)}{T(0)} \right) \]
\[ B = \frac{1}{D} \ln \left( \frac{T(\infty)}{T_{12}} \right) \]

where \( D \) = resist thickness
\( T(0) \) = initial transmittance
\( T(\infty) \) = final transmittance
\( T_{12} \) = air-resist interface transmittance = \( 1 - \frac{E_1}{E_2} \)

Measuring C

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

where \( T(0) \) = initial transmission
\( T_{12} \) = transmittance of the air-resist interface
\( T_{12} = 1 - \frac{E_1}{E_2} \left( 1 - \frac{E_1}{E_2} \right)^2 \)
\( E \) = incident dose

Measuring A, B, & C

- The best approach is to fit the measured \( T(E) \)
  curve with a numerical solution to the kinetic equations
- If \( A = 0 \), C cannot be measured in this way
- The Dill ABC parameters are also a function of wavelength
  - A and B can be easily obtained with a UV spectrophotometer
**Measuring A and B**

Resist A & B Parameters ($1/\mu m$)

**Wavelength (nm)**

<table>
<thead>
<tr>
<th>Wavelength (nm)</th>
<th>A</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>0.0</td>
<td>0.3</td>
</tr>
<tr>
<td>340</td>
<td>0.9</td>
<td>0.6</td>
</tr>
<tr>
<td>380</td>
<td>1.2</td>
<td>0.9</td>
</tr>
<tr>
<td>420</td>
<td>1.5</td>
<td>1.2</td>
</tr>
<tr>
<td>460</td>
<td>1.5</td>
<td>1.2</td>
</tr>
<tr>
<td>500</td>
<td>1.5</td>
<td>1.2</td>
</tr>
</tbody>
</table>

**Typical ABC Values**

- **G-line (436nm) Resist:**
  - $A = 0.6 \, \mu m^{-1}$, $B = 0.05 \, \mu m^{-1}$, $C = 0.015 \, cm^2/mJ$

- **I-line (365nm) Resist:**
  - $A = 0.9 \, \mu m^{-1}$, $B = 0.05 \, \mu m^{-1}$, $C = 0.018 \, cm^2/mJ$

- **248nm Resist:**
  - $A = 0.0 \, \mu m^{-1}$, $B = 0.50 \, \mu m^{-1}$, $C = 0.05 \, cm^2/mJ$

- **193nm Resist:**
  - $A = 0.0 \, \mu m^{-1}$, $B = 1.20 \, \mu m^{-1}$, $C = 0.05 \, cm^2/mJ$

- **Dyed Resist:**
  - $B$ value increased by 0.3 - 0.5 $\mu m^{-1}$

**Microscopic View of Exposure Kinetics**

- Exposure involves first absorption by the sensitizer, then reaction. The overall reaction rate constant can be related to the probability of absorption and the quantum yield:

  \[
  C = \Phi \sigma_{M-abs} \left( \frac{\lambda}{hc} \right) = \Phi \sigma_{M} \lambda \frac{N_A \hbar c}{\lambda} \]

  - $\Phi$ = Quantum yield (probability that an absorbed photon will yield an acid)
  - $\sigma_{M-abs}$ = Absorption cross-section of sensitizer
  - $\sigma_{M}$ = Molar absorptivity of sensitizer
  - $N_A$ = Avogadro’s number
  - $\hbar c/\lambda$ = Energy of one photon

**Resist ABC Review**

- Absorption and exposure can be described by the photoresist ABC parameters (Dill parameters)

  - The exposure kinetics of most photoresists are first order, giving an exponential dependence of chemical concentration on exposure dose with rate constant $C$.  

  - Positive value of $A$ means the photoresist bleaches (becomes more transparent) upon exposure

  - $B$ can be increased by adding an absorbing dye

**Lecture 50: What have we Learned?**

- What are the ABC parameters?
- How can one increase the value of $B$?
- How are the ABC parameters typically measured?
- What are typical values of $A$ for 248-nm and 193-nm resists?