EE-527: MicroFabrication

Negative Photoresists
A Little Structural Organic Chemistry - 1

alkanes: (no double bonds): \[
\begin{array}{c}
\text{H}_3\text{C} \text{--C--C--C--C--}
\end{array}
\]

alkenes: (at least 1 double bond): \[
\begin{array}{c}
\text{H}_3\text{C} \text{--C=\text{C--C--C--}}
\end{array}
\]

alkynes: (at least 1 triple bond): \[
\begin{array}{c}
\text{H}_3\text{C} \text{--C=\text{C=\text{C--C--}}}
\end{array}
\]

[alkenes and alkynes are unsaturated hydrocarbons.]
A Little Structural Organic Chemistry - 2

R—OH  alcohol
R—O—R'  ether  CH₃OH  methanol
R—CHO  aldehyde  HCHO  formaldehyde
R—C—R'  ketone  HCOOH  formic acid
R—C—OH  acid
R—C—O—R'  ester
R—O—OH  hydroperoxide
R—O—O—R'  peroxide
A Little Structural Organic Chemistry - 3

benzene

phenol

toluene

(ortho-) xylene

(meta-) xylene

(ortho-) xylene

(meta-) xylene

(paras-) xylene

ortho- means straight out
meta- means beyond
para- means opposite

R. B. Darling / EE-527
Common Monomers and Their Polymers - 1

**MONOMER**

- $\text{H}_2\text{C}=\text{CH}_2$
  - ethylene
- $\text{H}_2\text{C}=\text{CH}\quad \text{CH}_3$
  - propylene
- $\text{H}_2\text{C}=\text{CH}\quad \text{Cl}$
  - vinyl chloride
- $\text{H}_2\text{C}=\text{CH}$
  - styrene

**POLYMER**

- $[\text{H}_2\text{C}=\text{CH}_2]_n$
  - polyethylene (PE)
- $[\text{H}_2\text{C}=\text{CH}\quad \text{CH}_3]_n$
  - polypropylene (PP)
- $[\text{H}_2\text{C}=\text{CH}\quad \text{Cl}]_n$
  - polyvinyl chloride (PVC)
- $[\text{H}_2\text{C}=\text{CH}]_n$
  - polystyrene (PS)

R. B. Darling / EE-527
All rubbers are diene polymers
Common Monomers and Their Polymers - 3

D-glucose

D-manose

cellulose
## Atomic Weights

<table>
<thead>
<tr>
<th>Element</th>
<th>Atomic Weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>hydrogen</td>
<td>1.0079</td>
</tr>
<tr>
<td>carbon</td>
<td>12.011</td>
</tr>
<tr>
<td>nitrogen</td>
<td>14.0067</td>
</tr>
<tr>
<td>oxygen</td>
<td>15.9994</td>
</tr>
<tr>
<td>silicon</td>
<td>28.0855</td>
</tr>
<tr>
<td>sulfur</td>
<td>32.06</td>
</tr>
<tr>
<td>chlorine</td>
<td>35.453</td>
</tr>
</tbody>
</table>

(distribution of isotopes gives rise to fractional atomic weights)
### Molecular Weights

<table>
<thead>
<tr>
<th>Compound</th>
<th>Molecular Formula</th>
<th>Molecular Weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethylene</td>
<td>$\text{C}_2\text{H}_4$</td>
<td>$2(12.011) + 4(1.0079) = 28.05$ g/mole</td>
</tr>
<tr>
<td>Propylene</td>
<td>$\text{C}_3\text{H}_6$</td>
<td>$3(12.011) + 6(1.0079) = 42.08$ g/mole</td>
</tr>
<tr>
<td>Vinyl chloride</td>
<td>$\text{C}_2\text{H}_3\text{Cl}$</td>
<td>$2(12.011) + 3(1.0079) + 35.453 = 62.50$ g/mole</td>
</tr>
<tr>
<td>Styrene</td>
<td>$\text{C}_8\text{H}_9$</td>
<td>$8(12.011) + 9(1.0079) = 105.16$ g/mole</td>
</tr>
<tr>
<td>Methyl acrylate</td>
<td>$\text{C}_4\text{H}_6\text{O}_2$</td>
<td>$4(12.011) + 6(1.0079) + 2(15.9994) = 86.09$ g/mole</td>
</tr>
<tr>
<td>Methyl methacrylate</td>
<td>$\text{C}_5\text{H}_8\text{O}_2$</td>
<td>$5(12.011) + 8(1.0079) + 2(15.9994) = 100.12$ g/mole</td>
</tr>
<tr>
<td>Isoprene</td>
<td>$\text{C}_5\text{H}_8$</td>
<td>$5(12.011) + 8(1.0079) = 68.12$ g/mole</td>
</tr>
</tbody>
</table>

1 mole is Avogadro’s number of particles: $N_A = 6.023 \times 10^{23}$
Molecular Weight of a Polymer

• \( M_p = nM_m \)
  - \( n \) = number of units
  - \( M_m \) = molecular weight of monomer
  - \( M_p \) = molecular weight of polymer

• For use in a photoresist resin, need a molecular weight of around 100,000 - 200,000 for proper viscosity, melting point, softening point, and stiffness.

• Example:
  - To get \( M_p = 100,000 \) using isoprene (\( M_m = 68.12 \text{ g/mole} \)), need to get chains of average length of \( n = \frac{100,000}{68.12} = 1468 \) units.
  - This would lead to a molecule that is too long for proper photolithographic resolution, so need to coil the chains to make the lengths shorter and to increase the mechanical stiffness.
Polyisoprene Rubber

- 2-methyl-1,3-butadiene (isoprene) spontaneously polymerizes into natural latex rubber (polyisoprene).
- Polyisoprene becomes sticky and loses its shape at warm temperatures.
- Natural latex rubber is the only known polymer which is simultaneously:
  - elastic
  - air-tight
  - water-resistant
  - long wearing
  - adheres well to surfaces

\[
\begin{array}{c}
\text{polyisoprene} \\
\text{C}_5\text{H}_8
\end{array}
\]
Cyclicized Poly(cis-isoprene) - 1

- Poly(cis-isoprene) is the substrate material for nearly all negative photoresists.
  - cis- CH₃ groups are on the same side of the chain
  - trans- CH₃ groups are on alternatingly opposite sides of the chain
  - cis-isoprene is needed in order to curl the chains up into rings; (trans-isoprene will not work; CH₃ groups would hit each other).

- Two protons are added to cis-isoprene to further saturate the polymer and induce curling into cyclicized versions.

\[
\begin{align*}
\text{monocyclic poly(cis-isoprene)} & \quad \text{Bicyclic and tricyclic forms are also possible.} \\
C_{10}H_{16} & \quad \text{(This is usually part of the proprietary part of photoresist manufacture.)}
\end{align*}
\]
Cyclicized Poly(cis-isoprene) - 2

- Cyclicized poly(cis-isoprene) allows greater solids content in coating solutions and is less subject to thermal cross-linking.

<table>
<thead>
<tr>
<th>Property</th>
<th>Uncyclicized</th>
<th>Cyclicized</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average Molecular Weight</td>
<td>~ $10^6$</td>
<td>~ $10^4$</td>
</tr>
<tr>
<td>Density</td>
<td>0.92 g/mL</td>
<td>0.99 g/mL</td>
</tr>
<tr>
<td>Softening Point</td>
<td>28 C</td>
<td>50-65 C</td>
</tr>
<tr>
<td>Intrinsic Viscosity</td>
<td>3-4</td>
<td>0.36-0.49</td>
</tr>
<tr>
<td>Unsaturation</td>
<td>14.7 mmole/g</td>
<td>4-8 mmole/g</td>
</tr>
</tbody>
</table>
Vulcanization (Cross-Linking) of Rubber

- Vulcanization of rubber uses sulfur atoms to form bridging bonds (cross-links) between polymer chains.
- Sulfur is thermally activated; it is not photosensitive.

\[
\text{CH}_3 - \text{C} = \text{C} - \text{CH} - \text{C} = \text{C} - \text{C} = \text{C} - \text{C} - \text{S} - \text{S} - \text{S} - \text{S}
\]

R. B. Darling / EE-527
Components of a Negative Photoresist

1. Non-photosensitive substrate material
   - About 80% of solids content
   - Usually cyclicized poly(cis-isoprene)

2. Photosensitive cross-linking agent
   - About 20% of solids content
   - Usually a bis-azide ABC compound

3. Coating solvent
   - Fraction varies
   - Usually a mixture of n-butyl acetate, n-hexyl acetate, and 2-butanol

Example: Kodak KTFR thin film resist:
   - Work horse of the semiconductor industry from 1957 to 1972.
ABC Photosensitive Cross-Linking Agent

\[
\begin{align*}
\text{4-methylcyclohexanone} & \quad + \quad 2 \quad \text{4-azidobenzaldehyde} \\
\end{align*}
\]

\[
\begin{align*}
\text{2,6-bis(4-azidobenzal)-4-methylcyclohexanone} & \quad "\text{ABC}" \\
\end{align*}
\]
Bis-Azide Cross-Linking Agents

- “bis” means oppositely oriented---needed to attach both ends of the cross linker to two different substrate strands.
- It plays the same role as sulfur in vulcanization of rubber.
- The ABC bis-azide compound is photosensitive instead of being thermally activated.
- Photosensitivity arises from explosophore groups on ends:
  - N₃ azide group
  - NO₂ nitro group
  - Lead azide Pb(N₃)₂ is a primary explosive...
- Nitrenes are photoionized azide groups with a triplet ground state and a singlet excited state which is extremely reactive and capable of bonding to hydrocarbon chains.
Bis-Azide Cross-Linking Chemistry - 1

\[ R-N_3 \xrightarrow{\text{hv}} R-N^* + N_2 \]

photolysis of nitrene group: the only photoreaction

\[ R-N^* + HC \xrightarrow{1} R-N-C \]

\[ R-N + HC \xrightarrow{3} R-NH^* + \cdot C \]

\[ R-N + O_2 \xrightarrow{5} R-NO_2 \]

\[ R-NH^* + HC \xrightarrow{6} R-NH_2 + \cdot C \]
Bis-Azide Cross-Linking Chemistry - 2

– Photolysis of nitrene group by ultraviolet light is the only photoreaction.
– Reaction 1 is the desired pathway which leads to one end of the ABC compound being cross-linked to an isoprene strand.
– Reactions 2, 3, and 4 are an alternative pathway to the same result, involving an intermediate ground state and a radical state of the nitrene.
– The ground state nitrene can combine with O$_2$. (Reaction 5)
  • This competes with cross-linking.
  • This can be used in an image reversal process.
– The radical state nitrene can steal an additional proton from an isoprene strand and terminate the ABC compound without forming a cross link. (Reaction 6)
  • This competes with cross-linking, also.
Cross-Linking Efficiency

• $\chi$ is the efficiency of thermal cross-linking of nitrene groups to isoprene strands, set by the rates of reactions 1,2,3,4 versus 5,6.

• $\phi$ is the quantum efficiency of photolysis of the azide groups, set by the wavelength and absorption of the resist.

• $\Phi = \phi \chi$ is the quantum yield of cross-link bond formation.

• For a bis-azide resist, two bonds are needed (one on each end) to form a cross-link between isoprene strands; thus:
  
  • $\Phi = \phi^2 \chi^2$
    
    – This requires two photons per cross-link, and thus has very low photographic speed.
    
    – This allows great variety in the substrate polymer chains.
The Gel Point

- All sites for cross-linking (chromophores) are equally likely; thus, larger polymer chains are more likely to bind together than small ones.
- A many-branched supermolecule results from increased exposure.
- This supermolecule permeates the irradiated area forming a lattice which solvent atoms can penetrate, but not disperse.
- The polymer chains have at this point been rendered insoluble to the solvent, and the exposure required to produce this is called the Gel Point.
The Gel Curve

Gel Fraction, $W$

Exposure, $E$

(initial linear scale)

percent of solids by weight in a gel

Gel Point

Exposure is measured in Einsteins/cm$^2$

(1 Einstein = 1 mole of photons)

$\sim 5 \times 10^{16}$ photons/cm$^2$, or
$\sim 8.3 \times 10^{-8}$ Einsteins/cm$^2$
The Sensitometric Curve

- **Gel Fraction, \( W \)**
- **Exposure Dose, \( D \) (logarithmic scale)**

- **Gel Point**
- **Exposure energy dose in mJ/cm\(^2\)**

- **Percent of solids by weight in a gel**
- **Initial slope is the photographic contrast, \( \gamma \)**
- **Working point range**

\( D_G \sim 10-20 \text{ mJ/cm}^2 \)
Exposure and Dose Calculations

- \( N_A = \text{Avogadro's number} = 6.022 \times 10^{23} \text{ particles/mole} \)
- \( h = \text{Planck's constant} = 6.626 \times 10^{-34} \text{ J-s} \)
- \( c = \text{speed of light in vacuum} = 2.998 \times 10^8 \text{ m/s} \)

\[ N_A h c = 0.1196 \text{ J-m/mole} \]

- \( E = \text{exposure in Einsteins/cm}^2 \)
- \( D = \text{exposure energy dose in mJ/cm}^2 \)

Assume nearly monochromatic exposure illumination of wavelength \( \lambda \)

\[ \frac{hc}{\lambda} \] is the energy per photon

\[ \frac{N_A hc}{\lambda} \] is the energy in a mole of photons (one Einstein)

Therefore:

\[ D = \frac{EN_A hc}{\lambda} \]
Optical Absorption by the Resist

\[ A = \text{fraction of light that is absorbed by the photoresist layer} \]
\[ d_r = \text{thickness of the photoresist layer} \]
\[ \alpha_r = \text{optical absorption coefficient of the photoresist layer} \]
\[ \rho_r = \text{density of the photoresist layer} \]
\[ R_1 = \text{reflectivity of the air - photoresist boundary} \]
\[ R_2 = \text{reflectivity of the photoresist - substrate boundary} \]

single pass:

\[ A = (1 - R_1)(1 - e^{-\alpha_r d_r}) \]

double pass:

\[ A = (1 - R_1)(1 - e^{-\alpha_r d_r})[1 + R_2 e^{-\alpha_r d_r}] \]
Cross-Link Fraction

\[ E = \text{exposure in Einsteins/cm}^2 \]
\[ A = \text{absorbed fraction of light} \]
\[ \Phi = \text{quantum efficiency of cross-link formation} \]
\[ C = \text{cross-link fraction} \]

\[ EA\Phi = \text{number of formed cross-links in moles/cm}^2 \]

\[ d_r \rho_r = \text{mass of resist in grams/cm}^2 \]

\[ d_r \rho_r / 2M_m = \text{number of possible cross-links in moles/cm}^2 \]

therefore, the fraction of possible cross-links is proportional to the exposure:

\[ C = \frac{EA\Phi 2M_m}{d_r \rho_r} \]
Gel Point Exposure

• The gel point occurs when each polymer strand, on average, has one cross-link. Thus,

\[ C_{gel} = \frac{M_m}{M_p} = \frac{1}{n} \]

The gel point exposure is thus:

\[ E_{gel} = \frac{d_r \rho_r}{A \Phi 2 M_m n} = \frac{d_r \rho_r}{A \Phi 2 M_p} \]

For \( \Phi = 1, A = 1, d_r = 1 \ \mu m, M_p = 10^5 \ \text{g/mole}, \) and \( \lambda = 365 \ \text{nm}, \) obtain that

\[ E_{gel} = 0.25 \times 10^{-9} \ \text{Einsteins/cm}^2 \ \text{and} \ \ D_{gel} = 0.1 \ \text{mJ/cm}^2. \]

This is a benchmark for negative resist systems.

R. B. Darling / EE-527
The Flory Function - 1

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>( W )</td>
<td>gel fraction (fraction of solids)</td>
</tr>
<tr>
<td>( C )</td>
<td>cross-link fraction</td>
</tr>
<tr>
<td>( n )</td>
<td>degree of polymerization (an integer) = ( \frac{M_p}{M_m} )</td>
</tr>
<tr>
<td>( f(n) )</td>
<td>distribution of polymerization, a log-normal distribution</td>
</tr>
<tr>
<td>( \beta )</td>
<td>dispersity, typically 0.6 - 2.2</td>
</tr>
<tr>
<td>( n_0 )</td>
<td>average polymer chain length</td>
</tr>
</tbody>
</table>

The Flory function relates the cross-link fraction \( C \) (proportional to exposure) to the resulting gel fraction \( W \) (solids content) as a function of the average chain length and dispersity of the polymer.

\[
f(n) = \exp\left\{- \frac{(\ln n - \ln n_0)^2}{2\beta^2}\right\}
\]

\[
W = 1 - \frac{\sum_{n=1}^{\infty} n f(n) [1 - CW]^n}{\sum_{n=1}^{\infty} n f(n)}
\]
The Flory Function - 2

Gel Fraction, $W$

Exposure, $C/C_{gel}$

$\beta = 0$

$\beta = 1$

$\beta = 1.5$

$\beta = 2$
Dispersity and Contrast

• The slope of the sensitometric curve is the photographic contrast of the resist:

\[
\left( \frac{dW}{dE} \right)_{\text{gel point}} = \frac{2}{E_{\text{gel}}} e^{-\beta^2}
\]

\[
\left( \frac{dW}{d(\log E)} \right)_{\text{gel point}} = 2 \ln(10) e^{-\beta^2} = 4.606 e^{-\beta^2} = \gamma
\]

• Desire a minimally dispersed polymer to optimize the sensitometric curve.
  – Age increases the dispersity of the polymer.
  – This is a key factor in limiting the shelf life of photoresist.
Negative Photoresist Ingredients

• 1. Non-photosensitive substrate material
• 2. Photosensitive cross-linking agent
• 3. Coating solvent
• 4. Other additives: (usually proprietary)
  – antioxidants
  – radical scavengers
  – amines; to absorb O₂ during exposure
  – wetting agents
  – adhesion promoters
  – coating aids
  – dyes
The unexposed (uncross-linked) areas of resist as well as polymer chains that have not been cross-linked to the overall network of the gel must be dissolved during development.

Negative photoresist developers are solvents which swell the resist, allowing uncross-linked polymer chains to untangle and be washed away.

A sequence of solvents is often used to keep the swelling reversible.

The swelling of the resist during development is the largest contributor to loss of features and linewidth limitations.
Negative Photoresist Development - 2

Volume expansion factor, $V/V_0$

Increasing solubility parameter $\delta$

- Ethanol (base solvent)
- Hexane
- Toluene
- Benzene
- Chloroform

Molecular percent of solvent in ethanol

R. B. Darling / EE-527
Negative Photoresist Strippers

- Most commonly used are:
  - Methyl ethyl ketone (MEK)
  - Methyl isobutyl ketone (MIBK)
Single Component Negative Photoresists

- Electron beam irradiation produces cross-linking.
- An anion $A^-$ is needed to complete the reaction.

Glycidyl methacrylate and ethyl acrylate copolymer

$\text{glycidyl methacrylate and ethyl acrylate copolymer}$