Chemically Amplified Resist (CAR) - Exposure generates acid, but does not directly affect dissolution rate - Acid catalyzes a reaction during PEB (called amplification) which changes solubility - Important effects: acid diffusion and acid loss

**Exposure Reaction**

A Photoacid Generator (PAG) undergoes a photo-induced reaction to release a strong acid.

\[
\text{Ph} + \text{Ph} - \text{S}^+ \text{CF}_3\text{COO} \rightarrow h\nu \rightarrow \text{Ph} - \text{S}^+ \text{CF}_3\text{COOH} + \text{others}
\]

Triphenylsulfonium salt

(Simplified PAG and photogenerated acid)

**Amplification Reaction**

(during post-exposure bake, PEB)

\[
\text{CH}_2\text{-CH} \rightarrow \text{CH}_2\text{-CH} + \text{H}^+ \quad \Delta
\]

Polyhydroxy Styrene (PHS)

**Exposure**

Direct photon absorption by the PAG releases an acid in a first order reaction:

\[
\frac{\partial G}{\partial t} = -CGI \\
H = G_0 - G = G_0 \left(1 - e^{-CIH} \right)
\]

where

- \( G \) = PAG concentration
- \( G_0 \) = initial PAG concentration
- \( H \) = acid concentration
- \( I \) = intensity
- \( C \) = exposure rate constant
- \( t \) = exposure time

**Amplification**

The acid catalyzes a reaction which consumes a reactive site (protected/blocke d site) \( M \) to produce a reacted site (deprotected/deblocked site).

\[
\frac{\partial M}{\partial t_{PEB}} = -k_4MH \\
M = M_0 e^{-k_4H_{PEB}}
\]

where

- \( M \) = blocked site concentration
- \( M_0 \) = initial blocked site concentration
- \( k_4 \) = amplification rate constant
- \( t_{PEB} \) = bake time
Normalized Concentrations

- Concentrations can be normalized to initial values:

\[ h = \frac{H}{G_o} \quad m = \frac{M}{M_o} \]

\[ h = 1 - e^{-Ch} \]

\[ m = e^{-\alpha_f h} \]

where \( K_{amp} = G_o k_i \) = normalized rate constant

\( \alpha_f = K_{amp} \cdot PEB \) = amplification factor

Amplification Factor

- The amplification factor (\( \alpha_f \)) varies linearly with bake time
- It varies exponentially with temperature \( T \) through an Arrhenius equation

\[ K_{amp} = A_r e^{-E_a / RT} \]

where \( A_r \) = Arrhenius coefficient

\( E_a \) = Activation energy

\( R \) = Universal gas constant

Photon/Thermal Dose Trade-off

Lecture 51: What have we Learned?

- How are chemically amplified resists different from conventional (g-line and i-line) resists?
- What acts as the catalyst for the PEB amplification reaction?
- Why are these resist systems called “chemically amplified”?
- What are the two types of “dose” used to affect change in a CAR?