

CHE323/CHE384
Chemical Processes for Micro- and Nanofabrication
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Lecture 51
Lithography:
Chemically Amplified
Resists, part 1

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Chemically Amplified Resists

- Conventional Resist (g-line and i-line)
 - Exposure generates product which causes a direct change in the resist solubility
- 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

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Exposure Reaction

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

$$\begin{array}{c} \text{Ph} \\ | \\ \text{Ph}-\text{S}^+-\text{CF}_3\text{COO}^- \\ | \\ \text{Ph} \end{array} \xrightarrow{h\nu} \text{CF}_3\text{COOH} + \text{others}$$

Triphenylsulfonium salt

(Simplified PAG and photogenerated acid)

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Exposure

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

$$\frac{\partial G}{\partial t} = -CGI \qquad G = G_0 e^{-CI t}$$

$$H = G_0 - G = G_0 (1 - e^{-CI t})$$

where G = PAG concentration
 G_0 = initial PAG concentration
 H = acid concentration
 I = intensity
 C = exposure rate constant
 t = exposure time

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Amplification Reaction

(during post-exposure bake, PEB)

$$\begin{array}{c} \text{---CH}_2\text{---CH---} \\ | \\ \text{C}_6\text{H}_4 \\ | \\ \text{O} \\ | \\ \text{C=O} \\ | \\ \text{O} \\ | \\ \text{CH}_3\text{---C---CH}_3 \\ | \\ \text{CH}_3 \end{array} \xrightarrow[\Delta]{\text{H}^+} \left[\begin{array}{c} \text{---CH}_2\text{---CH---} \\ | \\ \text{C}_6\text{H}_3\text{(OH)} \end{array} \right]_n$$

Polyhydroxy Styrene (PHS)

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Amplification

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

If H is locally constant,

$$\frac{\partial M}{\partial t_{PEB}} = -k_4 M H \qquad M = M_0 e^{-k_4 H t_{PEB}}$$

where M = blocked site concentration
 M_0 = initial blocked site concentration
 k_4 = amplification rate constant
 t_{PEB} = bake time

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Normalized Concentrations

- Concentrations can be normalized to initial values:

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

$$h = 1 - e^{-Ct}$$

$$m = e^{-\alpha_f h}$$

where $K_{amp} = G_o k_d =$ normalized rate constant
 $\alpha_f = K_{amp} t_{PEB} =$ amplification factor

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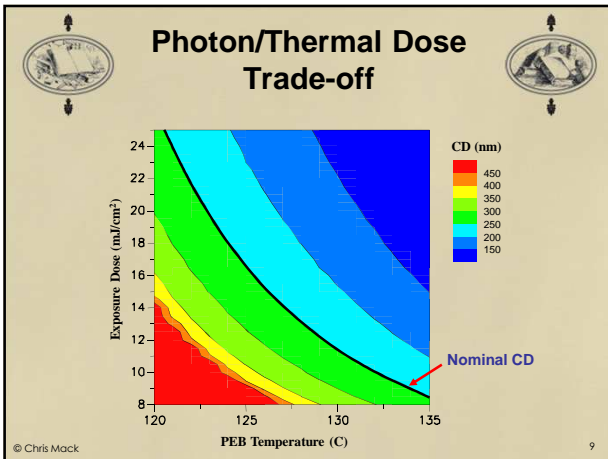
Amplification Factor

- The amplification factor (α_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

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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?

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