CHE323/CHE384
Chemical Processes for Micro- and Nanofabrication
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Lecture 50
Lithography: Photoresist ABCs

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Exposure Kinetics

- Photoresist exposure is first-order

$$\frac{dM}{dt} = -CIM$$

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

- If I is constant with time,

$$m = \frac{M}{M_o} = e^{-CIt}$$

M_O = Initial (unexposed) sensitizer concentration

Lambert Law of Absorption

- This is a well established empirical law:

$$\frac{dI}{dz} = -\alpha I$$

If α = constant,

$$I = I(z=0)e^{-\alpha z}$$

where I = Light intensity
z = Depth into the absorbing material
α = Absorption coefficient

Note: $\alpha = \frac{4\pi\kappa}{\lambda}$ where κ = 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,

$$\alpha = \Sigma\, a_i\, c_i$$

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,

$$\alpha = Am + B$$

$$A = (a_M - a_P)M_0 \qquad B = a_P M_0 + a_R R + a_S S$$

A = bleachable absorption coefficient
B = non-bleachable absorption coefficient
m = relative sensitizer concentration

Coupled Equations for Exposure

- Exposure Kinetics

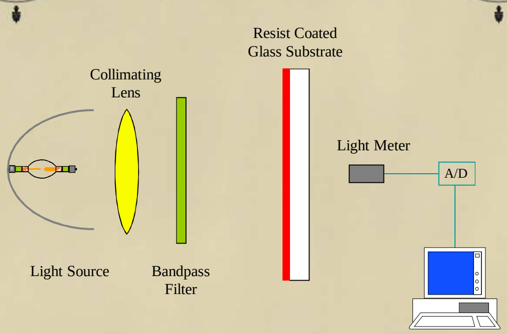
$$\frac{\partial m}{\partial t} = -CIm$$

- Absorption (non-reflecting substrate)

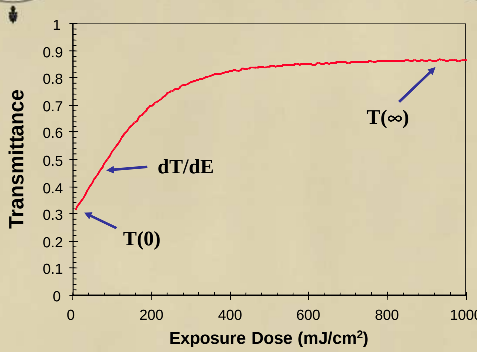
$$\frac{\partial I}{\partial z} = -(Am + B)I$$

ABC Parameters (also called Dill parameters)

Measuring the Dill ABC Parameters



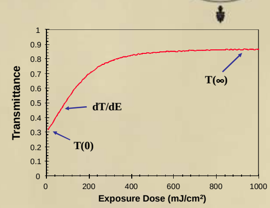
ABC Measurement



Measuring A and B

$$A = \frac{1}{D}\ln\left(\frac{T(\infty)}{T(0)}\right)$$

$$B = -\frac{1}{D}\ln\left(\frac{T(\infty)}{T_{12}}\right)$$



where D = resist thickness

$T(0)$ = initial transmittance

$T(\infty)$ = final transmittance

T_{12} = air-resist interface transmittance $= 1 - \left(\frac{n_2 - n_1}{n_2 + n_1}\right)^2$

Measuring C

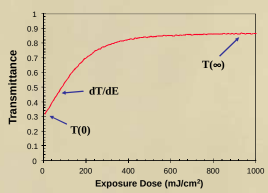
$$C = \frac{A+B}{A}\left(\frac{1}{1-T(0)}\right)\left(\frac{1}{T(0)}\right)\left(\frac{1}{T_{12}}\right)\frac{dT}{dE}\bigg|_{E=0}$$

where $T(0)$ = initial transmission

T_{12} = transmittance of the air-resist interface

$$T_{12} = 1 - \left(\frac{n_2 - 1}{n_2 + 1}\right)^2$$

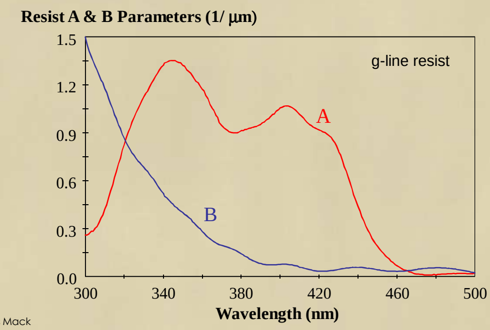
E = incident dose



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



Typical ABC Values

- G-line (436nm) Resist:
  - A = 0.6 µm^{-1}, B = 0.05 µm^{-1}, C = 0.015 cm^2/mJ
- I-line (365nm) Resist:
  - A = 0.9 µm^{-1}, B = 0.05 µm^{-1}, C = 0.018 cm^2/mJ
- 248nm Resist:
  - A = 0.0 µm^{-1}, B = 0.50 µm^{-1}, C = 0.05 cm^2/mJ
- 193nm Resist:
  - A = 0.0 µm^{-1}, B = 1.20 µm^{-1}, C = 0.05 cm^2/mJ
- Dyed Resist:
  - B value increased by 0.3 - 0.5 µm^{-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:

$$C = \Phi \sigma_{M-abs} \left(\frac{\lambda}{hc} \right) = \frac{\Phi a_M \lambda}{N_A h c}$$

Φ = Quantum yield (probability that an absorbed photon will yield an acid)
$\sigma_{M\text{-}abs}$ = Absorption cross-section of sensitizer
a_M = Molar absorptivity of sensitizer
N_A = Avogadro's number
hc/λ = 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?

