EE-527: MicroFabrication

Positive Photoresists

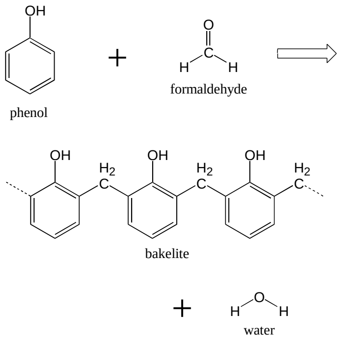
Advantages of Positive Photoresists

- Most commonly used in the IC industry.
- Superior to negative photoresists because:
  - They do not swell during development.
  - They are capable of finer resolution.
  - They are reasonably resistant to plasma processing operations.

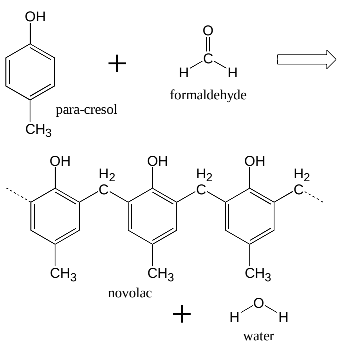
Phenolic Resins - 1

- Phenolic resins are condensation polymers of aromatic alcohols and formaldehyde.
- Bakelite was the first thermosetting plastic.
- Phenolic resins are readily cross-linked by thermal activation into rigid forms.
- Most phenolic resins are readily dissolved by aqueous alkaline solutions, e.g. NaOH, KOH, NH_4OH.

Phenolic Resins - 2



Phenolic Resins - 3



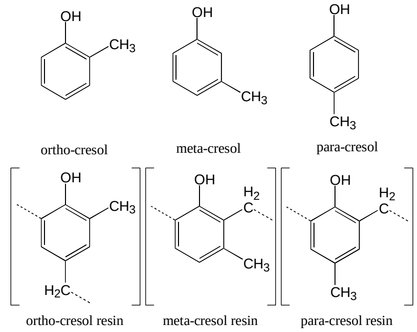
Important Properties of the Base Phenolic Resin

- average molecular weight
  - typically in the range of 1000 to 3000 g/mole
  - (8 to 25 repeating units in the polymer chain)
- dispersity of the molecular weights
- isomeric composition of the cresols
  - ortho-cresol
  - meta-cresol
  - para-cresol
- relative position of the methylene linkages ($--CH_2--$)

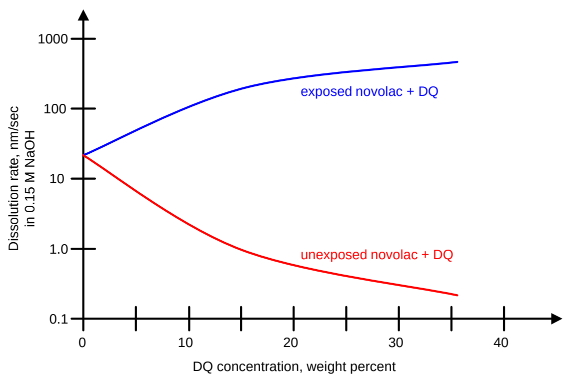
Dissolution of Phenolic Resins - 1

- Because of the OH groups, phenolic resins are hydrophylic and are readily dissolved by aqueous alkaline solutions.
- Diazonaphthaquinone (DQ) is a hydrophobic and non-ionizable compound.
- When phenolic resins are impregnated with DQ, they become hydrophobic and their dissolution is greatly inhibited.
- After exposure, DQ is converted into indene carboxylic acid (ICA) which is hydrophylic and very ionizable.
  - This allows the developer to wet and penetrate the novolac resin.
- Phenolic resins which contain ICA instead of DQ are readily dissolved by aqueous alkaline developers.

Cresol Isomers



Dissolution of Phenolic Resins - 2

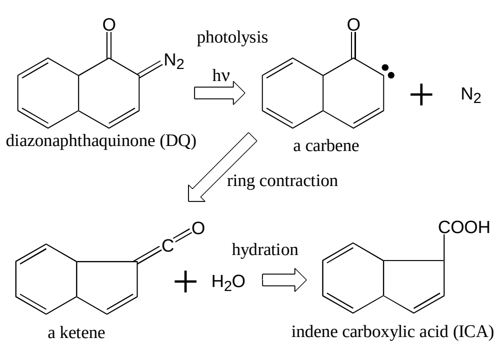


Cresol Isomer Properties

- Single isomers and smaller molecular weights are desirable
- Manufacture of positive photoresist relies heavily upon obtaining only a single isomer of the resin, usually para-cresol.
- Each monomer is $[C_8H_8O]$ (120.151 g/mole)

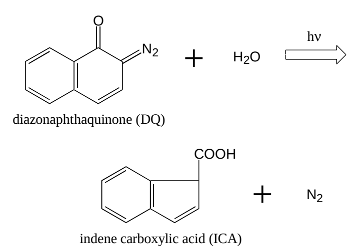
Isomer	Methylene Link	Molecular Weight	Dissolution Rate	Plastic Flow Temp.
ortho-cresol	3	2100 g/mole	2.7 A/sec	85 C
meta-cresol	1	15000 g/mole	0.7 A/sec	73 C
para-cresol	1	1600 g/mole	3.0 A/sec	119 C

DQ Primary Photoreaction



See Otto Suess, 1944 and 1947 papers in Annalen.

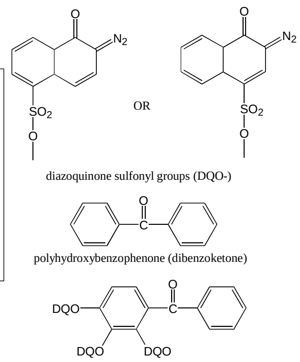
Photoreaction in a Positive Photoresist



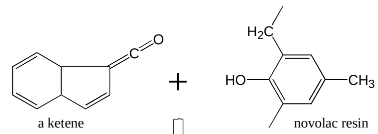
DQ Ballasting

Most positive photoresists use a derivative of the basic DQ photosensitive dissolution inhibitor. Diazoquinone sulfonyl groups (DQO) are added to a "ballast" compound such as dibenzoketone to produce a higher molecular weight compound such as tri-diazonaphthaquinone sulfonyl benzophenone

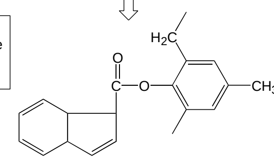
This is the most common photosensitive dissolution inhibitor which is used in common photoresist families such as AZ-1300, AZ-1500, AZ-4000, Microposit 1300, Microposit 1400, and Microposit 1800.



DQ Side Reactions - 1



Lack of humidity in a clean room will dehydrate the photoresist and promote this reaction.

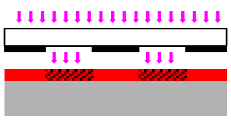


The ketene can form cross-links with the novolac if insufficient water is present-- just the opposite of what is desired...

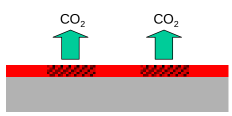
This is one reason why positive photoresist is so sensitive to humidity! Ketene scavengers, e.g. amines, are sometimes added to reduce this.

Positive Photoresist Image Reversal Process

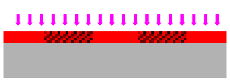
1. Standard masked exposure and conversion of DQ into ICA:



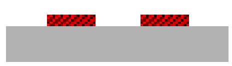
2. Baking and imidazole catalyst decarboxylates the ICA into indene:



3. Flood expose to convert the remaining DQ into ICA:



4. Development will dissolve away the regions which still contain ICA:



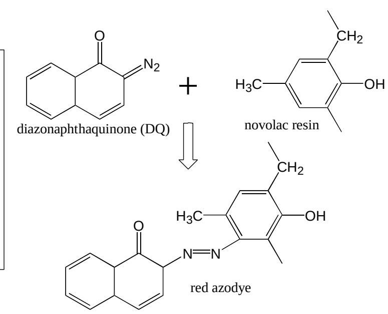
This is very useful when a negative image and an undercut resist profile are desired.

DQ Side Reactions - 2

This reaction always occurs to some extent, it causes the red color of photoresist, and it is benign as long as the DQ content is not overly depleted.

This reaction is more prevalent in the unirradiated areas where the DQ has not been consumed by the photolysis reaction.

This reaction is one of the basic shelf-life limits to positive photoresist.



Physical Requirements on the Photoactive Component

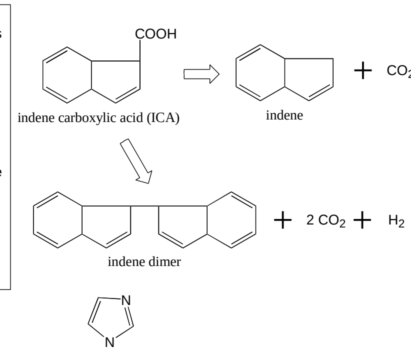
- Need an overlap of the absorption spectrum with the emission spectrum of the exposure source, e.g. a Hg lamp.
- Need bleachability at the exposure wavelength so that the photoreaction is able to reach the resist-substrate interface.
- Need compatibility with the base resin (novolac) so that the two form a single, miscible phase.
- Need thermal stability so that the photoactive dissolution inhibitor does not break down at prebake temperatures.
- Photoactive dissolution inhibitors are often modified to alter their spectral absorption, thermal stability, and miscibility characteristics.

DQ Side Reactions - 3

Decarboxylation of ICA occurs when the exposed photoresist is heated, and this usually occurs as a normal part of the process during postbake.

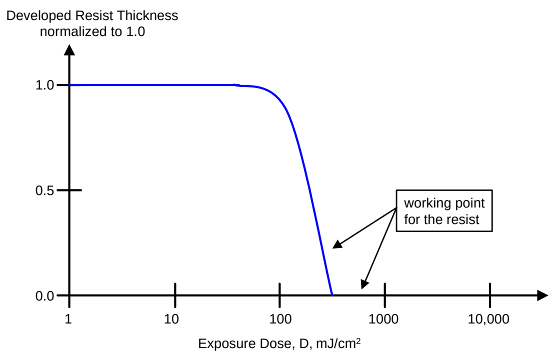
The decarboxylated indene or its dimer are both hydrophobic and non-ionizable, so these once again act as a dissolution inhibitor, although now they are no longer photosensitive.

This reaction can be used as the basis for an image reversal process, especially when it is catalyzed by a compound such as imidazole.



imidazole ($C_3H_3N_2$)

Sensitometric Curve for a Positive Photoresist



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Spectral Absorption of Novolac, DQ, and ICA

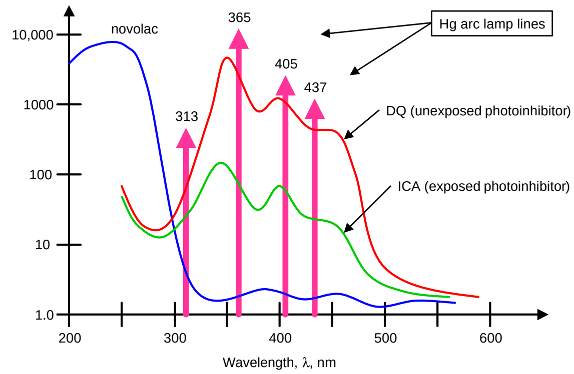

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Image Formation - The Dill Equations

- $M(z,t)$ = inhibitor fraction remaining
- $I(z,t)$ = radiation intensity

$$\frac{\partial M(z,t)}{\partial t} = -I(z,t)\,M(z,t)\,C$$

C expresses the photoreaction speed.

$$\frac{\partial I(z,t)}{\partial z} = -I(z,t)\left[A\,M(z,t) + B\right]$$

[AM(z,t) + B] plays the role of the optical absorption coefficient.

Initial Conditions:

$M(z,0) = 1$

$I(z,0) = I_0 e^{-(A+B)z}$

Boundary Conditions:

$I(0,t) = I_0$

$M(0,t) = e^{-I_0 Ct}$

The *{A,B,C}* parameters characterize a given positive photoresist.

This image formation model was developed by Fred Dill at IBM Corp.

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Primary Components of a Positive Photoresist

- Non-photosensitive base phenolic resin
  - usually novolac
- Photosensitive dissolution inhibitor
  - usually a DQ-derived compound
- Coating solvent
  - n-butyl acetate
  - xylene
  - 2-ethoxyethyl acetate
    - very carcinogenic, TLV = 5 ppm
    - now removed from most positive photoresists

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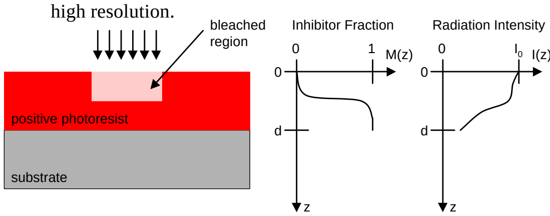
Bleaching of a Positive Photoresist

- The solution to the coupled Dill equations predicts a sharp boundary between exposed and unexposed regions of the resist. The boundary is the front of a bleaching edge which propagates downward to the substrate as the resist is exposed. This makes the wall angle more dependent upon the {A,B,C} Dill parameters than upon the exposure wavelength, and gives positive photoresists very high resolution.



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Secondary Components of a Positive Photoresist

- Antioxidants
- Radical scavengers
- Amines to absorb O_2 and ketenes
- Wetting agents
- Dyes to alter the spectral absorption characteristics
- Adhesion promoters
- Coating aids

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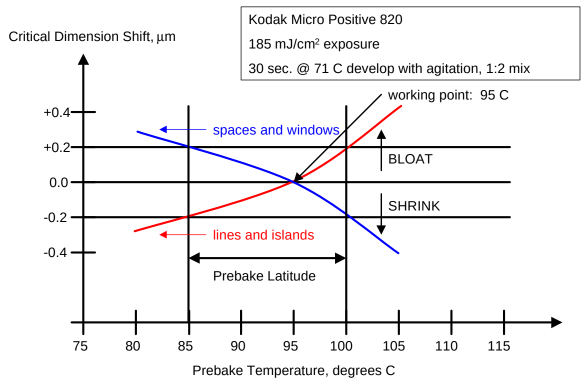
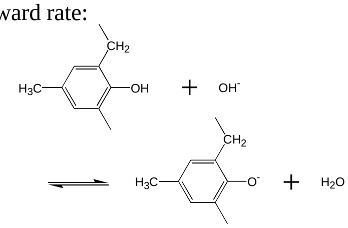
Positive Photoresist Prebake Latitude



Novolac Dissolution - 1

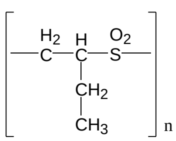
- A minimum concentration of [OH] is required to produce a net forward rate:



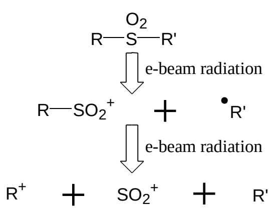
The dissolution rate is $R = kC^n$, where C is the base concentration.
For NaOH solutions, $R = (1.3 \times 10^5)\,[Na^+]^1\,[OH^-]^{3.7}$ Angstroms/second.

Single Component Positive Photoresists

- Use a photosensitive resin.
- Radiation produces chain scission, rendering region soluble to a developer.



polybutene-1-sulfone



Novolac Dissolution - 2

Typical data for different developer solutions:

Solution	Dissolution Rate, Angstroms/second	
	Unexposed	Exposed
0.15 M NaOH	20	1400
0.15 M KOH	10	860
0.15 M NaOH + 0.1 M Na_2SiO_3	270	3400
0.15 M NaOH + 0.1 M Na_3PO_4	350	2800
0.15 M NaOH + 0.1 M Na_2CO_3	270	2400

Positive Photoresist Exposure Latitude