DNQ Processing and Chemistry

• 1. Processing (book Chap 9)
• 2. DNQ Photoresist Composition (book Chap 8 pp 431 - 450)
• 3. DNQ Photoresist Exposure/PEB Development
• 4. Dills ABC parameters and modeling (book Chap 2 pp 128-130 & pp 531-535)
• 5. Dyed photoresist
• 6. Hardbake
• 7. Other http://www.finle.com/product_information/publications/

• Read: http://www.semiconductor.net/semiconductor/issues/issues/1999/sep99/docs/feature1.asp
DNQ Processing and Chemistry

1. Processing: Photoresist Key properties

- **Photospeed** is determined by the quantum efficiency of the resist, i.e., the ratio between the number of photoevents in the resist and the incident photon flux density.

- **Viscosity** affects the flow characteristics and film thickness, and depends on the solid content and temperature.

- **Adhesion** describes how strongly the film sticks to a broad range of substrate materials like silicon, oxide, nitride, polysilicon, and metals. Incomplete adhesion can cause a severe distortion or even the loss of a pattern.

- **Thermal stability** is necessary to withstand resist processing temperatures near 200 °C as well as additional plasma and UV treatment after the development.

- **Etch resistance** determines the ability of the film to protect the substrate from subsequent etching steps.

- **Contamination** of the resist by particulate and metal content increases the pinhole density.
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1. Processing: Photoresist Key properties continued

- **Shelf-life** refers to the storage time of the resist before unacceptable changes of its properties occur.

- **Pinhole density** expresses the number of holes per unit area created in the resist due to contaminants or inherent properties. In a thinner resist the pinhole density increases.

- **Charging** becomes important during plasma etching or deposition processes and ion implantation steps. The conductivity of the resist plays an important role for the charging rate.

- **Ease of processing** generally describes the complexity and difficulties to apply, develop, and strip the resist.
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1. Processing

- Clean Substrate
- Apply Adhesion Promoter
- Spin Coat
- Soft Bake
- Mask Alignment
- Resist Exposure
- Develop
- Postbake
- Descum
- Profile
- Etch
- Remove Photoresist
- Profile
- Repeat sequence for additional phase levels
DNQ Processing and Chemistry

1. Processing: Coating

![Graph showing spin speed vs. OiR 908-35, OiR 908-17, OiR 908-12](image)
DNQ Processing and Chemistry

1. Processing( DUV photoresist)

   - **Shipley UV5 DUV Photoresist Typical Process**

     - This resist has good plasma etch resistance (better than APEX-E). Resolution performance: For .5um thick resist: 0.2 um lines and spaces, 0.1um contact holes and 0.1um isolated lines.
     - **Singe** 150°C for 30 minutes
     - **HMDS prime** vapor for 60 sec at 120C
     - **Spin**: 5K RPM for 30 seconds = 5000A thickness
     - **Pre-bake**: hotplate 130°C for 1 minutes
     - **Expose**: 10 to 20 uC
     - **Post exposure bake** at 115°C for 90 seconds. (The PEB delay stability has been shown to be greater than 90 minutes up to 2 hours.)
     - **Develop**: 45 sec in LDD26W developer
     - **Hard Bake**: 145°C for 3 minutes
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1. Processing (DNQ I-line photoresist)

- 3612 resist Typical process
  - Dehydration bake : 30 minutes at 150°C
  - Prime : HMDS 60 sec vapor 120°C
  - Spin : spin 5.5K RPM, 30 seconds
  - Prebake: 90°C for 1 minute
  - Expose : 100 mj/cm²
  - Optional: Post Exposure Bake at 115°C for 1 minute (skip this step for >1μm resolution). Use the designated 115°C degree hotplate for this step. Doing this also improves the adhesion during wet etch (6:1 Buffered HF).
  - Develop: 60 seconds in LDD26W (2.38% TMAH)
  - Postbake: 110°C for 60 sec
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1. Processing Parameters

MASK (ω - dense/isolated lines or contacts)

AERIAL IMAGE projection system (λ, NA, σ)

LATENT IMAGE resist absorption
substrate reflectivity
PAC or PAG
diffusion/ PEB

RESIST PROFILE & IMAGE Resist type (dyes)
dissolution chemistry
development time

SUBSTRATE PROFILE & IMAGE etch or implant conditions
resist strip process
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1. Processing Parameters: Prolith

- Resist type (dyes)
- PAC or PAG diffusion/ PEB
- Substrates
- Substrate reflectivity
- Mask
  - $(\omega -$ dense/isolated lines or contacts)
- Projection system
  - $(\lambda, NA, \sigma)$
- Dissolution chemistry
- Development time
- Resist absorption
- Image in resist
DNQ Processing and Chemistry

1. Processing

Typical Depth of focus for DUV photoresist

X-sections through focus for 220nm L/s
DNQ Processing and Chemistry

1. Processing: Cauchy Coefficients

- Photoresist Cauchy Coefficients: Relate refractive index to wavelength (dispersion). \( n(\lambda) = A\nu + B\nu / \lambda^2 + X\nu / \lambda^4 \)
DNQ Processing and Chemistry

1. Processing: Cauchy Coefficients

- Photoresist Cauchy Coefficients: Relate refractive index to wavelength (dispersion). Used to measure thickness.
- The extracted Cauchy coefficients are valid for use at wavelengths of 400 nm to 800 nm. They correspond to the following dispersion relation:
  \[ n(\lambda) = A\nu + B\nu / \lambda^2 + X\nu / \lambda^4 \]

- **Shipley iline: Ultra i-120**
  - **193nm photoresist (no bleaching)**

<table>
<thead>
<tr>
<th>Cauchy coefficients</th>
<th>Unexposed</th>
<th>Bleached</th>
</tr>
</thead>
<tbody>
<tr>
<td>An</td>
<td>1.571</td>
<td>1.5921</td>
</tr>
<tr>
<td>Bn, nm²</td>
<td>0.017155</td>
<td>0.012132</td>
</tr>
<tr>
<td>Cn, nm⁴</td>
<td>0.0000086243</td>
<td>0.000172</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Cauchy coefficients</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>An</td>
<td>1.5246</td>
</tr>
<tr>
<td>Bn, nm²</td>
<td>0.003484</td>
</tr>
<tr>
<td>Cn, nm⁴</td>
<td>0.000149</td>
</tr>
</tbody>
</table>
DNQ Processing and Chemistry

2. DNQ Photoresist Composition

- Photosensitive polymer used for transferring pattern to substrate
- Has to
  - Adhere to substrate
  - Undergo radiation induced solubility change
  - Possess etch resistance
  - Be developable in aqueous base (or other solvent)
  - Disappear when not wanted
DNQ Processing and Chemistry

2. Photoresist Composition

*Courtesy George Barclay (Shipley)
DNQ Processing and Chemistry

2. Photoresist Composition
DNQ Processing and Chemistry

2. Photoresist Composition

• Key Idea: When each technology node changes active radiation wavelength (i.e. shorter), the photoresist resin has to change due to more absorption at shorter wavelengths:
  • I-line: 365nm Novolak resin
  • DUV: KrF 248nm: PHS
  • DUV: ArF 193 nm: Acrylic
  • DUV: F2 157nm: ??
# DNQ Processing and Chemistry

## 2. Photoresist Composition: Solvents

<table>
<thead>
<tr>
<th>Resist</th>
<th>Solvent in Shipley resists</th>
</tr>
</thead>
<tbody>
<tr>
<td>SPR2FX (g-line)</td>
<td>ethyl lactate</td>
</tr>
<tr>
<td>SPR-700 (gh-line)</td>
<td>80% ethyl lactate/13% anisole/7% iso-amyl acetate</td>
</tr>
<tr>
<td>SPR-500 (I-line)</td>
<td>90% ethyl lactate/5% n-butyl acetate/5% xylene</td>
</tr>
<tr>
<td>APEX-E (DUV)</td>
<td>100% propylene glycol/monomethyl ether acetate (PGMEA)</td>
</tr>
<tr>
<td>UV5 and 6 (DUV)</td>
<td>ethyl lactate</td>
</tr>
</tbody>
</table>
## DNQ Processing and Chemistry

### 2. Photoresist Composition

<table>
<thead>
<tr>
<th>Component</th>
<th>g-line 1</th>
<th>g-line 2</th>
<th>I-line</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resin</td>
<td>mature novolak, mixture of o, m, and p-cresols; differences in molecular wt. and poly-dispersivity</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PAC</td>
<td>2,1,5 PAC triester</td>
<td>2,1,5 PAC tetraester</td>
<td>2,1,5 PAC penta ester</td>
</tr>
<tr>
<td>Solids</td>
<td>27% solids/ 73% solvent</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Solvent</td>
<td>82%EGMEA</td>
<td>80% EL</td>
<td>90%EL</td>
</tr>
<tr>
<td></td>
<td>9%nBA</td>
<td>13% anisole</td>
<td>5%nBA</td>
</tr>
<tr>
<td></td>
<td>9%Xylene</td>
<td>7% amyl acetate</td>
<td>5%Xylene</td>
</tr>
</tbody>
</table>
DNQ Processing and Chemistry

2. Photoresist Composition: Novolak resin

Novolak resins have molecular weights of 500 to 20,000. They can be very linear or highly branched. Their molecular weight can be spread over a narrow range (i.e. $M_w/M_n =$ dispersivity or PD = 3-4) or a more broad range (i.e. PD >15).

**These factors determine the resin’s influence on the resist’s photospeed, thermal stability, resolution, process latitude, and etch resistance.**

This Novolak resin is an alkali soluble thermoplastic polymer. Named “novolac” by Leo Baekland from the use of resin in lacquers.
DNQ Processing and Chemistry
2. Photoresist Composition: Novolak resin

- Novolak resin is formed by reacting formaldehyde and excess phenol under acid catalysis. It is also called a phenol-formaldehyde resin. The polymer change length is governed by the amount of formaldehyde present.
- This chain length will changes the Novolak’s molecular weight, which effects photolithographic properties such as photospeed, resolution, and thermal resistance.
- Novolak resin is a clear yellow-orange resin when first manufactured, but darkens upon aging and appears reddish.
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2. Photoresist Composition: Novolak resin

- Novolak resin is formed by reacting formaldehyde and excess phenol under acid catalysis.

![Chemical reaction diagram showing the formation of novolac from formaldehyde and phenol.](image)
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2. Photoresist Composition: Novolak resin

- Novolak resin is made alkali-insoluble by the addition of
- hydrophobic diazo quinone PAC or DNQ
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2. Photoresist Composition: Novolak resin

- **Novolak resin physical characteristics:**
  - Brittle
  - Prone to form striations
  - Non-photosensitive
  - High solubility in basic solutions (pH>7.0)
DNQ Processing and Chemistry
2. Photoresist Composition: Novolak resin

- React Phenol/ or Cresol with Formaldehyde to create Resin (Novolak)
DNQ Processing and Chemistry

2. Photoresist Composition: Novolak resin

- React Phenol/ or Cresol with Formaldehyde to create Resin (Novolak) Properties

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

- Because of the OH groups, phenolic resins are hydrophylic and are readily dissolved by aqueous alkaline solutions.
## DNQ Processing and Chemistry

### 2. Photoresist Composition: Novolak resin

<table>
<thead>
<tr>
<th>Increase Novolak resin Parameter</th>
<th>Photospeed</th>
<th>Resolution</th>
<th>Thermal Resistance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular wgt. (Mw)</td>
<td>decreases</td>
<td>increases</td>
<td>increases</td>
</tr>
<tr>
<td>Ortho-Ortho Bonding</td>
<td>decreases</td>
<td>increases</td>
<td>increases</td>
</tr>
<tr>
<td>M-Cresol/Pcresol Ratio</td>
<td>increases</td>
<td>decreases</td>
<td>decreases</td>
</tr>
<tr>
<td>Dispersity (Mw/Mn)</td>
<td>decreases</td>
<td>decreases</td>
<td>increases</td>
</tr>
</tbody>
</table>
DNQ Processing and Chemistry

2. Photoresist Composition: DNQ

- Photo active Compound (PAC): DNQ

![Resonance forms of 2-diazo-1-oxo-naphthalene](image)

**Resonance forms of 2-diazo-1-oxo-naphthalene**
DNQ Processing and Chemistry

2. Photoresist Composition: DNQ

- Photo Active Compound (PAC): DNQ
- Note increased amounts of DNQ in a photoresist decreases the photospeed (i.e. requires a large exposure dose to convert all PAC.), increases resolution, and increases thermal resistance.

![Diagram of DNQ structures]

“2,1,5-" AND “2,1,4-" STRUCTURAL ISOMERS OF COMMON INHIBITORS
(R = BALLAST GROUP)
2. Photoresist Composition: DNQ

- For diazoquinone structures, the triester (T) and diester (D) sulfonic esters are more efficient inhibitors of developer dissolution than the monoester (M).
- Also higher ratios of $T > D > M$ will decrease the resist’s photospeed (i.e. more PAC’s need to be converted). Increased resist contrast can be achieved with various PAC ester ratios.

<table>
<thead>
<tr>
<th>Monoester</th>
<th>Diester</th>
<th>Triester</th>
</tr>
</thead>
<tbody>
<tr>
<td>(q=1)</td>
<td>(q=2)</td>
<td>(q=3)</td>
</tr>
</tbody>
</table>

![Chemical structures of monoester, diester, and triester](image-url)
DNQ Processing and Chemistry

2. Photoresist Composition: DNQ

: Q values

• Q = # PAC molecules attached to the Novolak resin.

• Note must expose (react) complete PAC molecule attached to a given Novolak resin chain for it to become soluble.

• Low PAC concentration = low effective q = high dissolution rate = low contrast = low resolution

• High PAC concentration = high effective q = low dissolution rate = high contrast = high resolution
DNQ Processing and Chemistry

2. Photoresist Composition: DNQ

: Q values = Must REACT ALL to be soluble!

From Shipley

\[
\text{Diazonaphthoquinone (DnQ)} \rightarrow 1) \text{Light} \rightarrow 2) \text{H}_2\text{O} \rightarrow \text{Indenecarboxylic acid (ICA)} + \text{N}_2
\]

DNQ = DIAZONAPHTHOQUINONE (DNQ)

I = INDENECARBOXYLIC ACID (ICA)

= Novolak Resin (R)
DNQ Processing and Chemistry

2. Photoresist Composition: DNQ

: Q values = Must REACT ALL to be soluble!

low PAC conc. moderate PAC conc. high PAC conc.
low effective q effective q=actual q high effective q

RESIN

PAC

extended PAC conc.
very high effective q
## DNQ Processing and Chemistry

### 2. Photoresist Composition: DNQ

<table>
<thead>
<tr>
<th>Increase PAC (DNQ) Parameter</th>
<th>Photospeed</th>
<th>Resolution</th>
<th>Thermal Resistance</th>
</tr>
</thead>
<tbody>
<tr>
<td>PAC concentration (Dill A value)</td>
<td>decreases</td>
<td>increases</td>
<td>increases</td>
</tr>
<tr>
<td>Composition (DNQ/OH ratio)</td>
<td>decreases</td>
<td>increases</td>
<td>increases</td>
</tr>
<tr>
<td>Hydrophobicity of ballast group</td>
<td>decreases</td>
<td>increases</td>
<td>N/A</td>
</tr>
<tr>
<td>Dye Concentration (Dill B value)</td>
<td>decreases</td>
<td>decreases</td>
<td>decreases</td>
</tr>
</tbody>
</table>
DNQ Processing and Chemistry

2. Photoresist Composition: DNQ

http://www.jsrmicroelectronics.com/download/spie95.pdf

Effect of DNQ concentration

From JSR SPIE 95

PHR = grams PAC (DNQ)/100 grams resin

Figure 7: 0.35μm line & space pattern profiles of resists with various DNQ contents. a)16PHR, b)20PHR, c)24PHR
3. DNQ Photoresist Exposure/PEB Development

- WOLFF REARRANGEMENT
- Exposure of DNQ to actinic radiation (Hg lamp: g-h-i lines) causes the photochemical conversion of the PAC into an acid (ICA) allows the developer to easily dissolve the now-un-inhibited resin.

After the PAC has been converted into the ketene and it’s reaction with water to form indene carboxylic acid, the PAC becomes hydrophilic, which permits better wetting by the aqueous developer.
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3. DNQ Photoresist Exposure/PEB Development

![Graph: i-line Ultra i-120 Optical Constants](image)
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3. DUV Photoresist Exposure/PEB Development

193 nm Resist Optical Constants

Index of refraction $n$

Extinction Coefficient $k$

Wavelength in nm

190 343 495 648 800
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3. DNQ Photoresist PEB

• Purposes: key idea
• DNQ/Novolak positive tone: diffusion bake: Diffusion of PAC to improve CD contact by removing standing waves.
• PAG/Novolak negative tone: (acid hardened resist: AHR) Diffusion of H+ ion to react with polymer causing polymer to become insoluble. (PAG: Triazine)
• DUV PAG/Blocking group/PHS: Diffusion of H+ ion to react with blocking group causing PHS to become soluble
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3. DNQ Photoresist PEB

• Standing waves can be smoothed out to improve CD control by a post exposure bake of DNQ photoresist to diffuse the PAC.

- Reflective surfaces below the resist can set up reflections and standing waves and degrade resolution.

- In some cases an antireflective coating (ARC) can help to minimize these effects. Baking the resist after exposure, but before development can also help.
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3. DNQ Photoresist PEB


- Standing waves can be smoothed by a post exposure bake

- Example of calculation of light intensity distribution in a photoresist layer during exposure using the ATHENA simulator. A simple structure is defined with a photoresist layer covering a silicon substrate which has two flat regions and a sloped sidewall. The simulation shows the [PAC] calculated concentration after an exposure of 200 mJ cm\(^{-2}\). Lower [PAC] values correspond to more exposure. The color contours thus correspond to the integrated light intensity from the exposure.

Same simulation example as above except that a post exposure bake of 45 minutes at 115 °C has now been included. The color contours again correspond to the [PAC] after exposure. Note that the standing wave effects apparent earlier have been “smeared out” by this bake, producing a more uniform [PAC] distribution.


DNQ Processing and Chemistry

3. DUV Photoresist Development

http://www.engr.washington.edu/~cam/PROCESSES/PDF%20FILES/PhotoresistPos.pdf

- Dissolution of photoresist in developer:

  - 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.
DNQ Processing and Chemistry

3. DUV Photoresist Development

http://www.engr.washington.edu/~cam/PROCESSES/PDF%20FILES/PhotoresistPos.pdf

- Dissolution of photoresist in developer:

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

\[
\begin{align*}
\text{H}_3\text{C} & \quad \text{CH}_2 \\
\text{H}_3\text{C} & \quad \text{CH}_2 \\
\text{O} & \quad + \\
\text{OH}^- & \quad + \quad \text{OH}^- + \text{H}_2\text{O}
\end{align*}
\]

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

3. DUV Photoresist Development

http://www.engr.washington.edu/~cam/PROCESSES/PDF%20FILES/PhotoresistPos.pdf

- Dissolution of photoresist in developer:

![Graph showing dissolution rate vs DQ concentration](image-url)
DNQ Processing and Chemistry

3. DUV Photoresist Development

http://www.engr.washington.edu/~cam/PROCESSES/PDF%20FILES/PhotoresistPos.pdf

- Dissolution of photoresist in developer: Old style Metal ion developers (NaOH) Contrast = dissolution rate exposed/ dissolution rate un-exposed

<table>
<thead>
<tr>
<th>Solution</th>
<th>Dissolution Rate, Angstroms/second</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Unexposed</td>
</tr>
<tr>
<td>0.15 M NaOH</td>
<td>20</td>
</tr>
<tr>
<td>0.15 M KOH</td>
<td>10</td>
</tr>
<tr>
<td>0.15 M NaOH + 0.1 M Na₂SiO₃</td>
<td>270</td>
</tr>
<tr>
<td>0.15 M NaOH + 0.1 M Na₃PO₄</td>
<td>350</td>
</tr>
<tr>
<td>0.15 M NaOH + 0.1 M Na₂CO₃</td>
<td>270</td>
</tr>
</tbody>
</table>
DNQ Processing and Chemistry

3. DUV Photoresist Development

http://www.engr.washington.edu/~cam/PROCESSES/PDF%20FILES/PhotoresistPos.pdf

- Contrast curve: threshold dose = photoresist clear point

![Contrast curve graph](chart.png)
3. DUV Photoresist Development

- AZO Dye: Dissolved novolak resin in the presence of the alkaline developer will react with non-converted PAC to form (via a diazonium azo-coupling reaction) an azo dye, sometimes referred to as the “red cloud”. The azo-coupling at the unexposed resist surface helps to provide good surface inhibition. Note that this reaction does however consume the developer and lower its activity. (from Shipley)
DNQ Processing and Chemistry

4. Dills ABC parameters and modeling

- Good website for modeling tutorial:
- http://www.iue.tuwien.ac.at/publications/PhD%20Theses/kirchauer/no
de4.html
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4. Dills ABC parameters and modeling

- Dill A: measure of the bleachable absorbance, is proportional to the diazonaphthoquinone content of the resist film.
- Dill B: measure of the non-bleachable absorbance, is proportional to the dye content plus the residual absorbance of the resist film.

Effect of increasing A:  
1) reduces the “swing ratio”
2) harms resist sidewall angle
3) at low dose will diminish reflective notching.

Effect of increasing B:  
1) will diminish reflective notching
2) reduces the “swing ratio”
3) harms resist sidewall angle
4) increases dose to size.
4. Dills ABC parameters:

**I-line Photoresist**

- **Before Exposure** $T(0)$
- **After exposure** $T(\text{infinity})$

- **I-LINE (365 nm)**
- **h-LINE (405 nm)**
- **g-LINE (436 nm)**
4. Dills ABC parameters : Transmission

- Transmission:
- Percentage of incident radiation passing through a given thickness of material.

\[ T = \frac{I_t}{I_0} \]

- \( I_t \) = Transmitted irradiance mw/cm²
- \( I_0 \) = Incident irradiance mw/cm²
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4. Dills ABC parameters : Absorption

- **Absorption** : Lamberts Law
- ( constant dye concentration)
- When radiation passes through an absorber, it’s irradiance is reduced.
  - \[ I = I_0 \, e^{-\alpha d} \]
- \( \alpha \) = absorption coefficient = \( 1/u \)
- \( d \) = thickness = \( u \)
- Transmission \( T = I_t/I_0 = e^{-\alpha d} \)

- **Optical density** \( D \) or Absorbance \( A \) :
  - \[ A = \log_{10} \left( \frac{1}{T} \right) = \log_{10} (O) \]
  - Opacity \( O = 1/T \) \( T = 10^{-A} \)
4. Dills ABC parameters : Absorption

- Absorption : Bouguers Law
- (constant dye concentration)
- When radiation passes through an absorber, it’s irradiance is reduced.
- \[ A = 0.4343 \alpha d \]
  \( \alpha \) = absorption coefficient = \( \frac{1}{u} \)
- \( d \) = thickness = \( u \)

- Absorption : Beers Law
- (variable dye concentration)
- When radiation passes through an absorber, it’s irradiance is reduced.
- \[ I = I_o e^{-\alpha cd} \]
  \( \alpha \) = molar absorption coefficient = \( \text{cm}^2/\text{mg} \)
- \( c \) = concentration of dye or absorber = \( \text{mg/cm}^3 \)
- \( d \) = thickness of film in cm
4. Dills ABC parameters : Absorption

- **COMPLEX REFRACTIVE INDEX**
- The absorption can be accounted for by the electrical field propagation through the material by using the complex refractive index of the material:
  - \[ n = n_r + i\kappa \]
  - \( n_r \) = real part of refractive index
  - \( \kappa \) = the extinction coefficient and accounts for absorption.

- Absorption coefficient \( \alpha = \frac{4\pi\kappa}{\lambda} \)
4. Dills ABC parameters and modeling

- Dill A: (note this is for a given wavelength!!)

- \( B = \text{Absorption coefficient } \alpha_{\text{exposed}} \)
- \( \alpha_{\text{unexposed}} = A + B \)

- \( A = \alpha_{\text{unexposed}} - \alpha_{\text{exposed}} \)

- Therefore:
  - \( A = \text{Absorption coefficient of bleachable material in photoresist} \)
  - \( 1/\mu m \)

- \( A = (1/d) \ln[T(\text{infinity})/T(0)] \)
DNQ Processing and Chemistry

4. Dills ABC parameters and modeling

Dill B: = Absorption coefficient of non bleachable material in photoresist 1/um

\[ B = -(1/d) \ln[T(\text{infinity})] \]

B increases as dye is added to photoresist
DNQ Processing and Chemistry

4. Dills ABC parameters and modeling

Dill C:  = bleaching rate = cm²/mJ

\[ C = A + \frac{B}{A I_0 T(0)[1-T(0)]} \times \frac{dT(0)}{dt} \]

\( d = \) photoresist thickness
\( T(0) = \) transmission at time 0 = unexposed photoresist
\( T(\text{infinity}) = \) transmission at time infinity = fully exposed photoresist

\( I_0 = \) intensity of incidence radiation
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4. Prolith Modeling

- Modeling Parameters for JSR PFR IX1010G I-line

- Prolith [Version] 6.0
  [Parameters]
  IX1010G ;Resist Name
  JSR ;Resist Vendor
  1 ;Read Only
  1 ;Resist Type (0=Negative, 1=Positive)
  0 ;Resist Type (0=Conventional, 1=Chemically Amplified)
  1 ;Number of Developers
  1 ;Dev model (1=Mack, 2=Enhanced, 3=Notch)
  PD523AD ;Developer Used
  134.0 ;Development Rmax (nm/s)
  0.04 ;Development Rmin (nm/s)
  0.44 ;Development Mth
  19.0 ;Development n
  0.10 ;Surface Development Rate
  500.000 ;Inhibition Depth (nm)
  34.320 ;Thermal Decomp. Ea(kcal/mole)
  36.800 ;Thermal Decomp. ln(Ar) (1/s)
  35.000 ;PEB Diffusivity Ea (kcal/mole)
  49.370 ;PEB Diffusivity Ln(Ar) (nm2/s)

;ABC data is in the following format:
;wavelength A B C Unexposed n Completely Exposed n
; (nm) (1/um) (1/um) (cm2/mJ)

[ABC Data]
365.000 a = 0.69 b = 0.06 c= 0.012 ;n unexposed = 1.70 ; n exposed = 1.70
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4. Prolith Modeling

- Modeling Parameters for PFR IX725D3G I-line dyed photoresist

- Version]6.0
  [Parameters]
  IX725D3G ;Resist Name
  JSR ;Resist Vendor
  0 ;Read Only
  1 ;Resist Tone (0=Negative, 1=Positive)
  0 ;Resist Type (0=Conventional, 1=Chemically Amplified)
  1 ;Number of Developers
  1 ;Dev model (1=Mack, 2=Enhanced, 3=Notch)
  PD523AD ;Developer Used
  76.600 ;Development Rmax (nm/s)
  0.011 ;Development Rmin (nm/s)
  0.210 ;Development Mth
  6.000 ;Development n
  0.400 ;Surface Development Rate
  0.530 ;Inhibition Depth (nm)
  34.320 ;Thermal Decomp. Ea (kcal/mole)
  36.800 ;Thermal Decomp. ln(Ar) (1/s)
  35.000 ;PEB Diffusivity Ea (kcal/mole)
  49.350 ;PEB Diffusivity Ln(Ar) (nm2/s)

;ABC data is in the following format:
;wavelength A B C Unexposed n Completely Exposed n
; (nm) (1/um) (1/um) (cm2/mJ)

[ABC Data]
365.000 0.5260 0.2450 0.0113 1.7200 1.7100
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5. Dyed photoresist

- Dill B parameter
- Dye is added to photoresist
- To absorb reflected rays
- From wafer substrate to
- Prevent:
- Reflective Notching:
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5. Dyed photoresist

• Reflective Notching:

The resulting photo-resist profile is shown below. The simulation of the non-planar effects demonstrates the impact of light scattering/interference on the linewidth.
DNQ Processing and Chemistry
5. Dyed photoresist

• Reflective Notching:
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5. Dyed photoresist

- Reflective Notching: one solution is adding a dye to the photoresist to allow absorption of the reflected ray so it is not as intense and will not expose. But addition of dye tends to cause sidewall angles to decrease.
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6. Hardbake

• A post develop bake is used to improve photoresist adhesion during wet chemical processing such as etch or plating.
• Also used to remove solvent from pattern to prevent “outgassing” during plasma etch or ion implant (i.e vacuum system processing).
• As mentioned earlier the thermal resistance of a photoresist is dependent upon the Novolak resin and the PAC.
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6. Hardbake

Photoresist thermal image distortion

![Image showing photoresist thermal image distortion with labels: No Hardbake, 120°C, 125°C, 130°C. The image indicates the effect of temperature on the photoresist structure.]
UV is radiated to the photoresist for hardening (curing) before the etching or ion implantation process. This enhances thermal resistance and plasma resistance of the photoresist, thus maintaining a good resist profile.
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7. Other Processes: Plateup:
Positive Vs Negative photoresist
Positive photoresist
DNQ Processing and Chemistry

7. Other Processes: Plateup:
Positive Vs Negative photoresist
Negative Photoresist
DNQ Processing and Chemistry

7. Other Processes: Plateup:
   Bump Process

(a) Plated Metal
   Photoresist

Metal Substrate

(b)