Is an EUV Film Quantum Yield of 30 Possible?

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Resist TWG
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Z-Parameter

\[ Z = D_0 \times LER^2 \times HP_{\text{min}}^3 \]

and \( LER^2 \sim \frac{1}{Q} \), so \( Z \sim \frac{1}{Q} \)

Gallatin et al., SPIE 2008
Gallatin, Naulleau, Brainard, SPIE 2007

For lower z parameter, increase quantum yield:

a) higher optical density (more photons absorbed)

b) better use of the energy from the photons that are absorbed
Electrons and Holes

Number of electrons per absorbed photon is about 2-4

Torok, Photopolymer S&T 2013
Kozawa SPIE 2008
De Schepper SPIE 2015

- Hole chemistry at most 4 reactions/photon
- Electron capture reaction at most 4 reactions/photon
- Use the rest of the energy loss events

92 eV (13.5 nm)

$hv$
Some Photo Acid Generators (PAGs)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>Norbornenedicarboximidyl triflate</td>
<td>NDT</td>
</tr>
<tr>
<td>Triphenylsulfonium triflate</td>
<td>TPS-OTf</td>
</tr>
<tr>
<td>Bis-(4-tert-butyl-phenyl)-iodonium; triflate</td>
<td>DTBI-OTf</td>
</tr>
<tr>
<td>Bis-(4-tert-butyl-phenyl)-iodonium; PFOS</td>
<td>DTBI-PFOS</td>
</tr>
</tbody>
</table>

Find the Weakest Bond!
Look for Bonds to Heteroatoms
Typical is 2-3 eV
Then 92 eV sufficient for more than 30 reactions!

<table>
<thead>
<tr>
<th>Bond</th>
<th>( \Delta H_{\text{bond}} ) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-H</td>
<td>4.3</td>
</tr>
<tr>
<td>C-C</td>
<td>3.6</td>
</tr>
<tr>
<td>O-O</td>
<td>2.0</td>
</tr>
<tr>
<td>C-S</td>
<td>2.8</td>
</tr>
<tr>
<td>C-I</td>
<td>2.2</td>
</tr>
<tr>
<td>N-O</td>
<td>2.4</td>
</tr>
</tbody>
</table>
Open-Source Photoresist: OS2

Our baseline material for most of this analysis is an Open Source Chemically Amplified Resist, Called OS2.*

This material was previously measured to have a quantum yield of 3 (3 acids produced per absorbed EUV photon)

*Higgins, Brainard et al. JJAP 50, 036504, 2011
Where does the energy go? 
look at ionization events

92 eV (13.5 nm)

Primary photon absorption 
(from CXRO website)
75% in polymer, 25% in PAG

Secondary electron ionization 
(from LESiS simulation software)
90% in polymer, 10% in PAG

For this material with 15% PAG, a little over 15% of ionization events in PAG
Is the other energy lost?
Polymer sensitization

For 193 nm exposures, polymer sensitization can increase quantum yield by 10x!

Cameron et al., SPIE 2001
Fedynyshyn et al., SPIE 2003
Fedynyshyn et al., SPIE 2008
And many others

http://chemwiki.ucdavis.edu/Core/Analytical_Chemistry/Instrumental_Analysis/Lasers
No clear indication of Polymer sensitization of PAG

Triphenylsulfonium Nonaflate

Grzeskowiak et al.,
Tuesday 8:40 AM 9979-10

Error bars are based on +/- 1 standard deviation from the mean.
How far does the photoelectron travel?

Includes Electron Trapping
When electron reaches 5 eV

Typical range about 3 nm for a primary 80 eV photoelectron

Narasimhan et al., Tuesday 9:40 AM 9979-13

15 wt.%
Are there enough PAG molecules present?

- Electron has net range of about 3 nm. How much volume of resist does the electron interact with?
- If assume approximately 3 nm diameter sphere, then 15 nm$^3$
- What about secondary electrons, do they add to the total volume or overlap same volume?
What is the Quantum Yield Limit?

Of course, first absorb as many photons as possible

Then, what are the limits to using those that are absorbed:

• Energy – sufficient for >30 reactions/photon
  • Use the energy for the right reactions

• Polymer absorption ~ 80% of ionization events
  • Find system with efficient energy transfer to PAG

• Number of electrons and holes ~4-8 per photon
  • Relevant if internal excitation not efficient process
  • Use material which generates more secondary electrons?

• PAG within path of electron ~10-20
  • Use higher PAG loading
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