Acid Generation in Chemically Amplified Photoresists

Part 1 – Thermal response
Jesus Barragan, David Gregory, Robert L. Brainard, Greg Denbeaux

Part 2 – Deuterated work
Steven Grzeskowiak, Michael Murphy, Sean Gibbons, Robert L. Brainard, and Greg Denbeaux

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IEUVI Resist TWG Meeting 2019

G. Denbeaux 02/24/2019
Part 1 – Thermally induced acid generation

Jesus Barragan, David Gregory, Robert Brainard, Gregory Denbeaux, SUNY Polytechnic Institute CNSE
Degas chamber

- High vacuum chamber <5E-8mbar
  - The EUV Technology RER300-PEX is an all metal, low hydrocarbon, UHV measurement chamber with loadlock, and a wafer transfer system that accommodates 300mm wafers.
- Halo 201 RC RGA by Hiden Analytical
  - Quadrupole mass spectrometer with SEM detector (mass range: 1-200amu)
  - 300mm carrier wafer and 2cm x 1cm photoresist coated test substrate (ESCAP thicknesses ~77nm)
    - The volume of a 77nm thick sample is equivalent to a 0.21nm thick residual layer on a 300mm wafer, and we easily detect that.
- Heat source: 1650W from Tungsten Halogen Bulbs
  - 650W under
  - 1000W above

Note – this is work in progress and our temperature measurements are not final
Photoresists

Poly (4-hydroxystyrene) and triphenylsulfonium nonaflate (without base)
PHS-TPS NF

Poly (methyl methacrylate)
PMMA

ESCAP and triphenylsulfonium nonaflate (without base)
ESCAP-TPS NF

ESCAP and diphenyliodonium nonaflate (without base)
ESCAP-DPI NF

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Identification of peaks

- The total outgassing pressure was calculated by summing up each mass pressure for all the scans during one heating cycle of ~200 seconds.

- The glowing masses will be shown versus temperature.

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Outgassing evolution of five photoresists due to heat

ESCAP-TPS NF (without base) signal vs temperature

PMMA signal vs temperature

ESCAP-TPS NF (with base) signal vs temperature

ESCAP-DPI NF (without base) signal vs temperature

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Where is the (lower temperature ~ 180 C) acid coming from?

Could it be from the PHS?

Next, compare PHS/TBA with PS/TBA

Acid from PAG

pKₐ=10

Deprotection from acid

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The PHS sample has a signature of acid catalyzed deprotection reactions near 180°C, and the PS sample doesn’t.

Yes – the presence of the PHS causes the deprotection reaction in the TBA.
Part 2 –
Acid generation – where is the H coming from?
(deuterated experiments)

Steven Grzeskowiak, Michael Murphy, Sean Gibbons,
Robert L. Brainard, Greg Denbeaux
SUNY Polytechnic Institute CNSE
Chemically Amplified Photoresist – OS4

PAG Decomposition in OS4.

\[
\text{PAG} + e^- \rightarrow \text{2Phenyl radical} \rightarrow \text{Phenyl radical} + \text{S}^- \rightarrow \text{Acid} + \text{X}^-
\]

Where is the hydrogen coming from within the resist??

- Typical outgassing shows 78 AMU so the phenyl radical gained a hydrogen from somewhere
- X- gains an H+ from somewhere to become an acid


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Resist Outgassing Exposure (ROX) Chamber - EUV

EUV (~ 92 eV) light

Expose

Detect outgassing components

C6

\[ + H^+ \rightarrow C6^+ \]
Acid Sensitive Dye – Coumarin 6

No measurable acid production for P3HT + PAG for doses as high as 10 mJ/cm².

However, outgassing evidence shows **PAG is decomposing!** (see next slide).

Acid production measured

No acid production measured
Why is the PAG decomposition species typically 77 AMU for P3HT vs 78 AMU for ESCAP – using the same PAG

Peak at 78 amu

Peak at 77 amu
Maybe the PHS has a role… again
Outgassing results (Peak AMU detected for phenyl)

NO effect from these samples from the deuterium (deuterated the wrong atoms…)

The presence of PHS correlates with the availability of hydrogen for phenyl radical to become benzene

But electron exposures (these are EUV) had anomalous results
Needs more exploration
Try modeling of the hydrogen bond energies - DFT with NWChem

\[ E_{1} \rightarrow E_{2} + H \cdot E_{3} \]

Calculate total energies for E1, E2, and E3 using DFT.

Then:

\[ E_{bond} = (E_{2} + E_{3}) - E_{1} \]
Carbon #6 was easiest to deprotonate, requiring 3.9 eV to remove a hydrogen.
Hydrogen 4, bonded to the tertiary carbon under the phenyl group was found to be the easiest to remove.

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<td>4.470</td>
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Parameters:
* Software: NWChem
* Method: DFT
* Basis Set: 6-31G*
The hydrogen on the hydroxyl group required the least amount of energy to remove, at 3.63 eV.

Parameters:
* Software: NWChem
* Method: DFT
* Basis Set: 6-31G*

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Conclusions

- Heating appears to cause acid generation directly from PHS - but likely a small contribution at typical bake temperatures.

- Where is the H coming from (phenyl radical -> benzene) and the H+ for the acid coming from?
  - Preliminary experiments indicate the hydroxide, at least for the phenyl radical -> benzene that we see in outgassing.
Acknowledgements

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- Jodi (Hotalen) Grzeskowiak
- Brian Taylor
- Kyle Unser
Appendix
Mechanisms of EUV Acid Generation - Literature

Isobutylene Outgassing Spectra

OS4 deprotection mechanism

\[
\begin{array}{c}
\text{OS4 deprotection mechanism} \\
\text{H}^+ \\
\Delta \\
\end{array}
\]

NIST Chemistry WebBook (http://webbook.nist.gov/chemistry)
### Raw Data

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