EUV Photoresists: What Needs to be Done?

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There is a Lot that Needs to be Done!

But There are Many Opportunities!
We Don’t Know Much About:

I. The Mechanisms of the Exposure of EUV Resists

We Have Not Reached the RLS Potential of EUV Resists:

II. Metal-Containing Resists Are the Best Solution to RLS.

III. What is the Best Way for EUV Resists to Reach their Full Potential?
Mechanisms of EUV Exposure are Very Complicated

\[ \text{C,H,O} + \text{EUV} \quad \text{hv} \quad 92 \text{ eV} \rightarrow \text{e-}/p^+ \]

How Many?

\[ \text{e-} (80 \text{ eV}) \rightarrow 2 \text{ eV} \]

- 80, 60, 40, 30, 20, 10, 5, 2 eV electrons probably behave completely different from each other.
- The electrons have very short life-times.
- The electrons cannot be detected or measured without leaving the film!
There is a Lot We Don’t Know

C,H,O + EUV
hv
92 eV → e-/p+

How many e-/p+ pairs do we make?

Can two e-/p+ pairs exist in the same time and space?

How far do e- go?

How is H+ generated from PAG?

What is the probability that e-/p+ pairs will recombine?
I.A. How Many Electrons?

2008: Is it possible to “Titrate” the number of e- using PAG?

Two PAG-Loading studies agree:
Quantum Yields of 5-6 $H^+$/Photon are possible.

Higgins & Brainard $^2$
Max $H^+ \Phi = 5.6$

Kozawa & Tagawa $^3$
Max $H^+ \Phi = 4.9$

3. Kozawa & Tagawa JJAP 2010 V. 49
I.A. How Many Electrons? By What Mechanisms?

Electron Trapping

\[ \text{e}^- + \text{PAG} \rightarrow \text{H}^+ \]  
\( (\Delta E = 2-3 \text{ eV}) \)

Hole-Initiated Chemistry

(Kozawa Mechanism)

\[ \text{p}^+ + \text{Polymer} \rightarrow \text{H}^+ \]

Our Current Thinking: Both of these mechanisms can occur independently.
I.A. Both Electron-Trapping and Hole-Chemistry Can Independently Create Acid

Electron-Trapping ~60%

Hole-Chemistry ~40%

Highest dose: 36 mJ/cm²

FQY = 5.1 ± 0.1

FQY = 3.1 ± 0.1

TPS-PFBS 15 wt.%

IEUVI-TWG 2020

Narasimhan, Grzeskowiak, Denbeaux & Brainard SPIE 2017
I.A. How Many Electrons per Absorbed Photon?

6 H+/Photon

Yields in Chemistry are ~70-100%

What Mechanism(s)?

- If e- only: Need 6-10 e-
- If p+ only: Need 6-10 p+
- If both e- and p+: Need 6-10 e-/p+ Pairs
- If either e- or p+: Need 3-5 e-/p+

How Many e/p+ Pairs?

Quantum Yield Triangle

Kozawa & Tagawa

Our Group

4. Narasimhan & Brainard SPIE 2017
Supports this conclusion
IB. How Far Do They Go?

E-Beam Depth Studies: Experiment and Modeling

- We used top down exposures and measure the depth to represent the lateral electron travel away from the EUV absorption site.
- We studied 2000, 700, 250 and 80 eV electrons.

Narasimhan, Grzeskowiak, Denbeaux & Brainard JM3 (2015)
Experiment:
Thickness Loss of Open-Source Resist

Direct Electron Exposure

Film Thickness

Thickness Loss (nm)

Dose (µC/cm²)

0.01 0.1 1 10 100 1000

0 10 20 30 40 50 60

15 wt.%
1.5 wt% TBAL

TBPI-PFBS

HOSyrt/Styr/TBA

C₄F₉SO₃⁻

2000 eV
700 eV
250 eV
80 eV

IEUVI-TWG 2020
I.B. Histograms from Modeling 100,000 Electrons vs. EUV Absorption Site

Number of Energy Loss Events per Electron per 0.1 nm vs. Depth in Resist (nm)

- 80 eV
- 250 eV
- 700 eV
- 2000 eV

Fully-Stochastic Monte Carlo Simulation Program: LESiS

Originally created by Leo Ocola and rewritten by our group: Narasimhan JM3 (2015).
I.B. Thickness Loss Simulation Results

Threshold set to match 700 eV simulation and experimental data

2000 eV

700 eV

Low-Energy Transitions
I.B. Thickness Loss Simulation Results

Threshold set to match 700 eV simulation and experimental data

250 eV

80 eV

Ionization: \( e^- \)  
Plasmon Generation: \( e^- \)
I.B. What is Missing from Our Model?

(2) Ionization:
\[ \Delta E = 10-12 \text{ eV} \]
Binding Energy

(4) Plasmon Generation:
\[ \Delta E = 3-24 \text{ eV} \]

Electron Trapping
\[ e^- + \text{PAG} \rightarrow H^+ \]
\[ \Delta E = 2-3 \text{ eV} \]

Energy-Loss Events

Plasmon

Ionization

5 eV

(CSDA)
Continuous Slowing-Down Approximation

Count when Electrons “Fall below 5 eV”

Thanks to Liam Wisehart
I.B. Thickness Loss Simulation Results

Threshold set to match 700 eV simulation and experimental data

A better model when 3 or 5 eV transitions are included.

Ionization: \[ e^- \rightarrow e^- \]

Plasmon Generation: \[ e^- \rightarrow e^- \]

Low-Energy Transitions
I.C. Do Multiple e-/p+ Pairs Coexist in Time and Space?
I.D. Can an e- Fall into Another $h_{\nu}$ Hole?

In order to answer this question we must know:
1) The arrival rates of photons (We Know)
2) The cross-section for electron/hole recombination (vs. e- energy) (Don’t Know)
3) The lifetimes of the electrons and holes (Don’t Know)
I.C. Electron Energy vs. Travel Time

200 EUV photons on OS2

Average time between arrival of photons in 100 x 100 nm area

*Photoelectron escaped into vacuum

Can’t Co-Exist; Can’t Interact

Modelled by LESiS
I.E. Conclusions about Mechanisms

Five Key Questions:

• How many electrons are made?
  Our opinion: 3-5 e-

• By what mechanisms is acid generated?
  Our opinion, both electron-trapping and hole-initiated reactions occur independently.

• How far do electrons travel?
  2-5 nm. Our modeling matches our experimental results.
  Better question: How far do they travel and still react?

• Do Multiple e-/p+ Pairs Coexist in Time and Space?
  No—by at least 3 orders of magnitude

• Can an e- Fall into Another h ν’s Hole?
  They don’t coexist, so probably not.
II. 2011-2012: Oregon State and Cornell University

**Hafnium-Oxide Resists**

- **OSU/Inpria\(^1\)**
  - 20-nm lines

- **Cornell\(^2\)**
  - 36-nm h/p lines
  - 12 mJ/cm\(^2\)

**Improve resist stochastics by incorporating metals with high EUV absorptivity (Thackeray).\(^3\)**

Molecular Organometallic Resists for EUV (MORE)

Our group wrote a proposal to Intel to look at the rest of the periodic table.
II. Motivations for Metal-Based Resists
(Inpria Resist Design Principles)

- Small Building Blocks
- High Absorbance
- High Material Homogeneity
- Low Electron Blur
- High Etch Selectivity

High selectivity etch directly into SOC
II. Wide Process Window for Inpria SnOx Resists on NXE-3300

Logic: 13 nm HP L/S

- Large Process Window
- Printable to < 10 nm L/S
- DtS: 33 mJ/cm²
- DOF > 200 nm (10% EL)
- $E_{L_{\text{max}}}$: 22%
- LWR: 3.4 nm

DRAM: 40 nm Pitch Dense Pillars

- DtS: 52 mJ/cm²
- LCDU: 2.4 nm
- DOF > 140 nm
- $E_{L_{\text{max}}}$: >30%
II. Mono-Nuclear Tin Carboxylates with Remarkable LER

Del Re, et al., JM³ (2015)
II. Antimony MORE Resists

We discovered this resist system in 2014. One of its remarkable features is that development in either water or hexanes yields negative-tone imaging.
II. Metal-Containing Resists: Overview

- Inpria started with HfOx resists and is now manufacturing SnOx resists, that are under evaluation in fabs around the world.

- CNSE has explored multiple platforms, targeting highly absorbing metals.

- The Major Advantages of Metal-Containing Resists Are:
  - Increased absorbance for better photon stochastics.
  - Single-component systems for better homogeneity.
  - Smaller molecular size.
  - Huge etch resistance.
III. Can Metal-Based Resists Replace CAR’s in Some Applications?

*I think it is inevitable.*

If So, Why Hasn’t It Happened Already?

It’s Complicated…

- Metal-Fab Integration Issues
- Redesign of Manufacturing Protocols
- Many New EUV Exposure Mechanisms

But I don’t think CAR to MOx is as complicated as 193-nm to EUV.
III. Industrial Experience:
CAMP vs. Metal-Containing Resists

- DUV 193-nm EUV

1. Industrial Experience of CAMP vs. Metal

- 36 years x 90% Market/Research
- 32 Industry-Years

- 10 years x 3% Market/Research
- 0.3 Industry-Years

- Roughly 100:1

- Metal-Containing Resists

- 2008

References:
1. Ito, Willson, Frechet CAMP Pat. App.
2. Kunz et al. SPIE
3. Brainard - Resist to EUV-LLC
4. Stowers - MNE
III. What is the Best Way for EUV Resists to Reach their Full Potential?

Sematech is Gone….

Fundamental Understanding of:

• Mechanisms of Traditional CAMP Resists Remain Poorly Understood.
• New Metal Resists Need to be Discovered.
• Each new Metal Resist will have a Separate Mechanism.

Billions of $$ have been spent to develop the Physics and Engineering of EUV.

This industry needs to find a way to support research in the chemistry of EUV resists.
IV. Acknowledgements

SUNY Polytechnic Institute (CNSE)  
Professor Greg Denbeaux

Students:
Amrit Narasimhan  Steven Grzeskowiak
Michael Murphy  Brian Cardineau
James Passarelli  Jodi Hotalen

Paul Scherrer Institut (EUV Exposures)
Michaela Vockenhuber  
Yasin Ekinci

Inpria
Stephen Meyers
Jason Stowers
Andrew Grenville

BMET Team
Patrick Naulleau
Chris Anderson

Sematech
Mark Neisser
Stefan Wurm
Chandra Sarma
Appendix
II. How Many Electrons: Chemical Mechanisms

Thackeray\textsuperscript{18} and Kozawa\textsuperscript{2} think that EUV resists need \textit{both} phenolic polymers and electron trapping to generate acid.

(18) Thackeray \textit{et al.} SPIE 2013
(2) Kozawa \textit{et al.} SPIE 2010
Possible Mechanism of Electron-Trapping

\[ \text{Ph}_3\text{S}^+ + \text{e}^- \rightarrow \text{PhS}^+ \rightarrow \text{Half an antibond} \]

\[ \text{Ph}_2\text{S} + \text{Ph} \rightarrow \text{R} + \text{PhH} + \text{Ph}_2\text{S} \rightarrow \text{H}^+ + \text{R} \]

\[ \text{H}^+ + \text{Ph} \rightarrow \text{PhOH}_2 \rightarrow \text{H}^+ \]

\[ \text{H}^+ + \text{Ph}_3\text{S}^+ \rightarrow \text{H}^+ + \text{PhS}^+ \]
II. Fully-Stochastic Monte Carlo Simulation Program: LESiS

Input Data and Theory from ‘56-’85 gas phase experiments.

Key Assumptions:

• The gas phase work applies to EUV.
• Plasmons do not generate electrons.
• Continuous Slowing Down does not generate electrons


Photoelectron:

EUV hv

Yeh et al. (1985)

Ionization:

Gryzinski et al. (1965)
Vriens et al. (1964-69)

Plasmon Generation:

Ferrel (1956)
Quinn et al. (1962)

Elastic Scattering:

ΔE = 0

Mott & Massey (1965)
II. Fully-Stochastic Monte Carlo Simulation Program: LESiS

V. Can Metal-Based Resists Replace CAR’s in Some Applications?

Gregg Gallatin: 
RLS trade-off

\[ LER \propto \frac{1}{\sqrt[3]{\alpha Q E R}} \]

Absorbance

Target transmission for EUV resists is 50%. 
James Thackeray, SPIE 2011 Plenary Presentation

At film thickness of 20 nm, PHS will only stop 10% of photons.
I.C. Electron Travel Time (LESiS)

Distribution of Electron Travel Time

- 10^4 EUV photons on OS2 for each data set
- Average time between arrival of photons in 100 x 100 nm area
- Time between EUV Pulses

Modelled by LESiS