EUV resist: the great challenge of small things

S. Castellanos

EUVL Workshop 11-14 June 2018, Berkeley
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Motivation

“Can we define common targets and goals in a roadmap for the whole EUV resists community? Unlike the case of the EUV scanner, there are multiple parties working on resists but no general consensus.”

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Historic trends of EUV resists
What do we know about mechanisms in EUV resists?
What do we not know about EUV resists?
How are we going to make resists ready?
Table of contents

- What is needed from photoresists?
- Where are we?
  - Historic trends of EUV resists
  - What do we know about mechanisms in EUV resists?
  - What do we not know about EUV resists?
- How are we going to make resists ready?
Where are we?

Line/space roadmap in literature

## Requirements according to literature

<table>
<thead>
<tr>
<th></th>
<th>Dose (mJ/cm²)</th>
<th>( \mu ) (( \mu m^{-1} ))</th>
<th>LWR 3( \sigma ) (nm)</th>
<th>LER 3( \sigma ) (nm)</th>
<th>PSD(0)</th>
<th>defectivity</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>&lt;20(^{[1,2,3,4]})</td>
<td>15*(^{[5]})</td>
<td>&lt; 20%(^{[4]})</td>
<td>&lt; 12-15% CD(^{[2,3]})</td>
<td>???</td>
<td>pixNOK (space) = 10^{-5}(^{[5]}) VIA failure &lt; 10^{-12}(^{[1]})</td>
</tr>
</tbody>
</table>

## Some of best reported performances

<table>
<thead>
<tr>
<th></th>
<th>Dose (mJ/cm²)</th>
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</tr>
</thead>
<tbody>
<tr>
<td>CAR (CD = 16 nm)(^{[6]})</td>
<td>45</td>
<td>5</td>
<td>2.91</td>
<td>2.01</td>
<td></td>
<td>pixNOK &lt;D.L. (10^{-7})</td>
</tr>
<tr>
<td>CAR (CD = 13 nm)(^{[2]})</td>
<td>58</td>
<td>5</td>
<td>4.4</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>nCAR (CD = 16 nm)(^{[2]})</td>
<td>47.5</td>
<td>20</td>
<td>4.0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>nCAR (CD = 13 nm)(^{[2]})</td>
<td>34</td>
<td>20</td>
<td>3.8</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PSCAR(^{[7]})</td>
<td>37.5 (15 J/cm² UV)</td>
<td></td>
<td>1.94</td>
<td>25.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>IM(^{[8]})</td>
<td>38.5</td>
<td></td>
<td></td>
<td>3.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>not specified(^{[4]})</td>
<td>21.4</td>
<td></td>
<td></td>
<td>5.2</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Calculated for the requirement of OD = 36% in a 30 nm photoresist

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Where are we?

Line/space roadmap in literature

Half Pitch / nm

LER (3σ) / nm

2016 2018 2020 2022 2024 2026 2028 2030

"10"
"7"
"5"
"3"
"2.1"
"1.5"
### Requirements according to literature

<table>
<thead>
<tr>
<th>Dose (mJ/cm²)</th>
<th>μ (μm⁻¹)</th>
<th>LWR 3σ (nm)</th>
<th>LER 3σ (nm)</th>
<th>PSD(0)</th>
<th>defectivity</th>
</tr>
</thead>
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### Some of best reported performances

| CAR (CD = 16 nm)[^6] | | | | | |
|-----------------------|---|---|---|---|
| CAR (CD = 13 nm)[^2] | 58 | 5 | 4.4 | | |
| nCAR (CD = 16 nm)[^2] | 47.5 | 20 | 4.0 | | |
| nCAR (CD = 13 nm)[^2] | 34 | 20 | 3.8 | | |
| PSCAR[^7] | 37.5 (15 J/cm² UV) | | 1.94 | 25.7 |
| IM[^8] | 38.5 | | 3.7 | |
| not specified[^4] | 21.4 | | 5.2 | |

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* Defectivity decreases with absorptivity!![^5,^9]*

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[^1]: Calculated for the requirement of OD = 36% in a 30 nm photoresist
What is needed from EUV resists?

It is not only about decreasing $3\sigma$.

*Chris A. Mack, IEUVI Resist TWG meeting, Feb. 25 2018*
Table of contents

• What is needed from photoresists?

• Where are we?
  • Historic trends of EUV resists
  • What do we know about mechanisms in EUV resists?
  • What do we not know about EUV resists?

• How are we going to make photoresists ready?
Historic trends

Historic trends

P. Naulleau, Frontiers Nanoscience 2016
What do we know?

Chemically amplified resists (CAR)

- e-cascade induced reaction
- H+ catalysis

Non-chemically amplified inorganic resists (nCAR)

- e-cascade induced reaction
What do we know?

**CAR**

**New formulations:**
- Enhanced absorptivity
- Decreased acid diffusion
  - Covalently bonded PGA
  - Higher $T_g$ (JSR)

**Molecular based:**
- Well defined structure => LER
- Tuneability

**PSCAR**
- More sensitive
- Improved contrast in latent image

**Multitrigger (Irresistible materials)**
- Improved contrast in latent image

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**nCAR**

**Sn-based Inpria molecular materials:**
- High absorptivity ($20 \, \mu m^{-1}$)
- Sensitivity

**Nanoparticles:**
- Ober
  - High sensitivity ($<3 \, mJ/cm^2$)
  - High LER
- Inpria (peroxide HfOx)
  - High sensitivity

**MORE (Brainard):**
- Sn-based
  - Low LER ($2.1 \, nm \, CD = 16 \, nm$)
  - 600 $mJ/cm^2$
- Other metals
  - High sensitivity ($5.6 \, mJ/cm^2$, 35 nm Pitch)

**MOCs (Castellanos, Ober)**
- Sensitivity tuned by metal content
- LER scumming

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General concerns:
- Absorption of EUV photons
- Resolving low CDs

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What do we know?

Electron uptake generates acid \((5.6/\text{photon})^{[1]}\)

- Playing with IP of polymer (more secondary electrons)
- Playing with EA of PAGs\(^{[1,2]}\)

Reminder:

High contribution of photoelectrons from the valence band! (80 eV)


Our playground as chemists
What do we know?

PSCAR®

Proc. of SPIE (2016), 9776, 977607

Irresistible Materials®

Proc. of SPIE 2018, 10583, 1058308
What do we know?


- At 5 nm CARs fail too much[1]
- At lower node CARs cannot operate[1]
- Chemical stochastics in the range of photons stochastics[2]

### Main issues

- Roughness (PSD)
- Defectivity (NOK)

### Claims

- At 5 nm CARs fail too much[1]
- At lower node CARs cannot operate[1]
- Chemical stochastics in the range of photons stochastics[2]

---

What do we know?

- **Inorganic core** defines the **absorption** and **photoelectron yield**
- **Organic shell** defines the type of **chemistry** and the **secondary electron yield**

Work in progress in ARCNL:
- > absorption tuning with metal
- > promoting electron-induced cleavage in ligands
- > low ionization potential
Can we find some guidelines with so many variables??

...well, there are some features in common

Polymer based:
- Increased absorptivity (F?, metals (JSR))
- Decreased acid diffusion

Sn-based molecular materials:
- Increased absorptivity
- Sensitivity??

More sensitive
- Improved contrast in latent image
- Number of absorbed EUV photons?

Multitrigger (Irresistible materials)
- Improved contrast in latent image
- Absorptivity
- CD

MORE (Brainard):
- Low LER!
- High sensitivity (??)

MOCs (Castellanos, Ober)
- Molecular control
- Cross-linking of shell
Historic trends of EUV resists

What do we know about mechanisms in EUV resists?

What do we not know about EUV resists?

How are we going to make photoresists ready?
Some personal thoughts

- Electrons above IP generates electrons
- Electrons below IP interact resonantly with the molecules => need of potential curves
- Contribution of holes??
What we do not know?

Currently at ARCNL: chemistry of secondary electrons

Photoemission Electron Microscope (PEEM)

Measures the electrons that are created by the absorbed x-rays.

X-ray adsorption

Chemical information

Soft X-rays

PEEM

electrostatic lenses

Sample

screen

NEXAFS Spectrum

Photon Energy [eV]

275  280  285  290  295

NEXAFS C-K Edge 283.3  285.7

[\text{a.u.}]

\frac{I_{\text{ref}}}{I_{\text{exp}}}.

Without exposure

Photon Energy [eV]

485  490  495  500

NEXAFS Sn-M Edge 488.9  493.1  497.2

[\text{a.u.}]

\frac{I_{\text{ref}}}{I_{\text{exp}}}.

Without exposure

Photon Energy [eV]
Gain fundamental knowledge

**Photoelectron yield (Auger, valence)** [Ogletree]

Study of low energy electrons:
- Cross-sections for specific reactions
- **Secondary electrons per photoelectron** [Thete, 2017 PRL]
- Mean free paths

**Improvement on current systems**

**Increase solubility contrast/sensitivity**

**Decrease of defects**
- Absorption
- Photoelectron yield
- More effective chemistry (hole, electron induced)
- Play with underlayer

**Breakthrough!!**

- Use the knowledge on:
  - Photoelectrons yield
  - Secondary electrons
  - Electron and hole chemistry for **new concepts**.

2018 2019 2020

HP = 7nm!!
New concepts

Simplify systems
- Smaller and more dense units: metal halogens?
- Rule out multiple components with random distribution: CAR, ligand exchange

Separating absorption and chemical events
- Layer of dense and ordered metal absorbers
- Use of hot electrons to do chemistry on resist
  - Thin film resists with high etching resistance:
    - Promoting a change in the oxidation state of the underlayer to switch etching resistance
- Avoid development? (volatile inert products?)

Introducing anisotropy
- Propagation of the image only perpendicular to the plane (less shot noise)

"Transforming" high energy electrons in low energy electrons
- Electron scattering through layer that yields plasmons/hot electrons

(*similar idea by AZ Electronic Materials Manufacturing, Proc SPIE 2014, 9051, 905117)
A roadmap should be proposed in the photoresist community to set targets and priorities. This should cover:

- Roadmap of photoresist performance

- Fundamental understanding of EUV induced processes, with main emphasis in **low energy electrons induced chemistry and stochastics**
  - Ionization potential, amplification of secondary electrons
  - Resonant processes (electron attachment reactions)
  - Chemistry of radical anions (thermalized electrons)
  - Modeling (molecule specific)
• Currently, there are many attractive strategies to improve the performance of EUV resists:
  ▪ Boosting non-linear response (PS-CAR, Irresistible materials)
  ▪ Simplifying systems: molecular resists with metal content (Inpria, MORE, metal oxoclusters)

• **Disruptive designs are needed within the next 2 coming years to fight stochastics and the SLR trade-off.** Some ideas:
  ▪ Anisotropy
  ▪ Separating absorption and electron-induced chemistry
  ▪ Narrowing electron energy distribution (valence band electrons always there!)
• Vivek Bakshi
• Harry Levinson
• Anindarupa Chander
• Danilo de Simone
• Yasin Ekinci
• Wim van der Zande
• Claire van Lare

Thanks for your attention!
What is needed from EUV resists?

<table>
<thead>
<tr>
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<tr>
<td></td>
<td>1H</td>
<td>2H</td>
<td>1H</td>
<td>2H</td>
<td>1H</td>
<td>2H</td>
</tr>
<tr>
<td>GlobalFoundries</td>
<td>14LPP</td>
<td>7nm</td>
<td>7nm</td>
<td>with EUV*</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Intel</td>
<td>14 nm</td>
<td>14 nm+</td>
<td>14 nm++</td>
<td>10 nm</td>
<td>10 nm+</td>
<td>10 nm++</td>
</tr>
<tr>
<td>Samsung</td>
<td>14LPP</td>
<td>10LPE</td>
<td>10LPP</td>
<td>8LPP</td>
<td>7LPP</td>
<td>6 nm* (?)</td>
</tr>
<tr>
<td>SMIC</td>
<td>28 nm**</td>
<td></td>
<td>14 nm</td>
<td>in development</td>
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<tr>
<td>TSMC</td>
<td>CLN16FF+</td>
<td>CLN10FF</td>
<td>CLN7FF</td>
<td>CLN12FFC/CLN12ULP</td>
<td>CLN7FF+</td>
<td>5 nm* (?)</td>
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<td>UMC</td>
<td>28 nm**</td>
<td>14nm</td>
<td>no data</td>
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</tbody>
</table>

*Exact timing not announced
**Planar