LER Degradation vs. EUV Resist Thickness
Report for Technical Working Group

Brian Cardineau,¹ William Earley,¹ Tomohisa Fujisawa,² Ken Maruyama,³ Makato Shimizu,² Shalini Sharma,³ Karen Petrillo,⁴ Mark Neisser⁴ and Robert Brainard¹

1. College of Nanoscale Science and Engineering, University at Albany
2. JSR Corporation
3. JSR Micro Inc.
4. SEMATECH, Albany, NY

Funded by SEMATECH

I. Introduction
II. Substrate Interaction
III. Optical Density
IV. PAG Segregation (Acid Diffusion)
V. Glass-Transition Temperature
VI. Summary and Conclusions

See full SPIE Paper 8322-7: Cardineau Monday 4PM
I. As Resolution Improves, Resist Thickness must Decrease to Prevent Line Collapse, However, LER Gets Worse!

Four resists all show same problem.

50 nm L/S
Model for LER vs. Film Thickness

Keddie Model for Tg as a function of film thickness:

\[ T_g(d) = T_g(\infty) \left[ 1 - \left( \frac{A}{d} \right)^{\delta} \right] \]


CNSE Model for LER as a function of film thickness:

\[ LER(d) = LER(\infty) \left[ 1 + \left( \frac{A'}{d} \right)^{\delta'} \right] \]

- \( T_g(\infty) = \) Bulk Tg
- \( A' = \) Thickness Dependence
- \( \delta' = \) Exponential
- \( \phi = \) Area under LER curve
  (Larger \( \phi \) → Worse LER thickness dependence)
Model for LER vs. Film Thickness

Keddie Model for Tg as a function of film thickness:

\[ T_g(d) = T_g(\infty) \left[ 1 - \left( \frac{A}{d} \right)^\delta \right] \]

CNSE Model for LER as a function of film thickness:

\[ LER(d) = LER(\infty) \left[ 1 + \left( \frac{A'}{d} \right)^{\delta'} \right] \]

- \( T_g(\infty) = \) Bulk Tg
- \( A' = \) Thickness Dependence
- \( \delta' = \) Exponential
- \( \varphi = \) Area under LER curve
  (Larger \( \varphi \) \( \rightarrow \) Worse LER thickness dependence)

LER Limits of Resist Thin Films

Determine the root cause of the degradation of LER vs. thickness in EUV resists by studying this phenomenon as a function of resist:

- Substrate Interaction
- Optical Density
- PAG Segregation (Acid Diffusion) New since Vote
- Glass Transition Temperature (Tg)

Please get ready to vote on your favorite!
Which *characteristic* plays the greatest role in the *mechanism* of the Thin-Film LER Problem?

A) Resist Optical Density  
B) Resist Glass-Transition Temperature  
C) Resist Substrate (ie Underlayer)  
D) All of the Above (no bet)  
E) None of the Above (no bet)

**Vote Occurred Last Year at RMAG/SPIE 2011**
Which *characteristic* plays the greatest role in the *mechanism* of the Thin-Film LER Problem?

**March RMAG Votes**

1. Resist Optical Density 4
2. Resist Glass-Transition Temperature 4
3. Resist Substrate (ie Underlayer) 5
4. All of the Above 2
5. None of the Above 1 (TW)

Dan Sullivan (IBM):

“Much more complicated than we can possibly understand”
Today’s ReVote:

Which *characteristic* plays the greatest role in the *mechanism* of the Thin-Film LER Problem?

A) Resist Optical Density
B) Resist Glass-Transition Temperature
C) Resist Substrate (i.e. Underlayer)
D) PAG Attachment (Acid Diffusion)
Two Resists as a Function of Thickness

Primed Silicon

Underlayer\(^2\)

\(^1\)Model resist was provided by JSR. \(^2\)Commercial Organic EUV underlayer.
Two Resists on Two Substrates

For both resists in this study, using an organic underlayer does not significantly effect the LER thickness problem ($\phi$).

$^1$Model resist was provided by JSR.  $^2$Commercial Organic EUV underlayer.
III. Resist Optical Density: Fluoropolymer Set

Objective: Vary Optical Density without drastically changing the resist chemistry.

Calculated Optical Density*

<table>
<thead>
<tr>
<th>Thickness</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td>90</td>
<td>0.18</td>
<td>0.21</td>
<td>0.27</td>
<td>0.28</td>
</tr>
<tr>
<td>60</td>
<td>0.12</td>
<td>0.14</td>
<td>0.18</td>
<td>0.19</td>
</tr>
<tr>
<td>40</td>
<td>0.08</td>
<td>0.09</td>
<td>0.12</td>
<td>0.12</td>
</tr>
<tr>
<td>30</td>
<td>0.06</td>
<td>0.07</td>
<td>0.09</td>
<td>0.10</td>
</tr>
<tr>
<td>20</td>
<td>0.04</td>
<td>0.05</td>
<td>0.06</td>
<td>0.07</td>
</tr>
</tbody>
</table>

* Optical Densities of Full Resists: 15% DTBPI Nf PAG and 1.5% TBA Lactate Base. Calculations were made using empirical formula and a density of 1.2 g/mL using CXRO Website.
LER vs. Thickness and vs. Optical Density

50 nm CD

LER (nm) vs. Thickness (nm)

40 nm CD

LER (nm) vs. Thickness (nm)

OD @ 90 nm

0.18

0.21

0.27

0.28

Chemical structures A, B, C, and D are shown with their respective OD values.
Increasing Optical Density using Fluorinated Monomers:

- Causes a degradation in LER
- Causes the LER thickness problem (φ) to get ~3X worse.

This correlation is **contrary** to what has been predicted by some researchers.
IV. PAG Segregation

Fluorinated PAGs are known to segregate to resist surfaces.

This stratification can cause surface inhibition, and flatter resist tops. (Less top-loss)

Could changes in the concentration of PAG at the surface be responsible for poorer imaging in thin films?
Polymer Bound PAG vs. Blend

Model Resists Provided by JSR:

Resist A (Blend):  
Lower PAG Diffusion

Resist B (Bound):  
Higher PAG Diffusion

Resists A and B have a comparable polymer.
The Effect Bound PAG has on LER Limitation

Binding the PAG to the polymer appears to significantly improve the LER thickness problem ($\varphi$), improving by a factor of $\sim 3X$ for both feature sizes.
V. Glass-Transition Temperature: Systematic Study of Polymer Tg on LER/Thickness Problem

Prepare High & Low Tg polymers and determine:
• LER vs. thickness.
• Acid-diffusion length (EL) vs. thickness

* Tg values in brackets are modeled results. Bicerano, “Prediction of polymer properties” / Fox Tg
Lithographic Evaluation Through Thickness of 5 Resists of Varied Tg

Tg (at 60 nm)

- A: 147°C
- B: 144°C
- C: 126°C
- D: 112°C

**50 nm CD**

**36 nm CD**

**LER (nm)**

**Thickness (nm)**
Tg vs. Film Thickness

Keddie Equation:

\[ T_g(d) = T_{g\infty} \left[ 1 - \left( \frac{A}{d} \right)^{\delta} \right] \]

<table>
<thead>
<tr>
<th>Resist</th>
<th>( \varphi_{Tg} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>488</td>
</tr>
<tr>
<td>B</td>
<td>295</td>
</tr>
<tr>
<td>C</td>
<td>182</td>
</tr>
<tr>
<td>D</td>
<td>29</td>
</tr>
</tbody>
</table>

Comparison of Tg Results

LER vs. Film Tg for all Thicknesses

φ_{LER} vs. Tg

φ_{Tg} vs. Tg

φ_{LER} vs. φ_{Tg}

φ_{LER} is proportional to φ_{Tg}!
VI. Conclusions

![Graph showing LER (at 90 nm) vs. Substrate Interaction, Optical Density, PAG Segregation, Glass Transition Temperature.](image)

- **Substrate Interaction**: Range: [0.1]
- **Optical Density**: Range: [3.9]
- **PAG Segregation**: Range: [1.8]
- **Glass Transition Temperature**: Range: [1.4]

![Graph showing \( \Phi_{\text{LER}} \) (nm²) vs. Substrate Interaction, Optical Density, PAG Segregation, Glass Transition Temperature.](image)

- **Substrate Interaction**: Range: [21]
- **Optical Density**: Range: [78]
- **PAG Segregation**: Range: [82]
- **Glass Transition Temperature**: Range: [55]
VI. Conclusions
Summary

Substrate Interaction:
• There is no significant change in $\phi$ for either substrate.

Optical Density:
• Both LER and $\phi$ get worse with increasing Fluorine content and optical density.

PAG Segregation/Acid Diffusion Control:
• $\phi$ improves by a factor of ~3 when the PAG is polymer bound.
• Winner!

Glass Transition Temperature:
• $\phi$ seems to correlate with both Tg and gets worse with higher Tg.
• We will determine acid diffusion for each polymer at each thickness using the C/H method described by Chris Anderson.
Acknowledgements

Project Funding By:

EUV Imaging:
Staff at BMET
Staff at EMET

Donation of Monomers:
Central Glass
Dow Chemical

Ellipsometry:
Alain Diebold

Group Members Past and Present:

Justin Torok
Avyaya Jayanthinarasimhan
Patricia Wolf
Craig Higgins
Seth Kruger
Appendix
Increasing Optical Density using Fluorinated Monomers:
- Causes a degradation in LER
- Causes the LER thickness problem ($\varphi$) to get ~3X worse.

This correlation is contrary to what has been predicted by some researchers.
Underlayer Interaction

There is an established relationship between LER and substrate CTE.

32 nm L/S - BMET

Silicon

CTE (ppm)

LER (nm)

A)

30 nm L/S
LER = 4.8

With HMDS

With Underlayer

60 nm resist thickness

LER
Δ 20%

Thickness

Does this improvement hold true through thickness? Can an UL fix LER in ultra thin films?
One theory is that the thin-film LER problem is *due to* decreased *total* absorption.

If so, how does the resist top know that it is thinner?

Is making thinner films darker a solution?
V. Glass-Transition Temperature

Tops of resist profiles are very different in thin films.

Tg Changes Dramatically at thin films.

Are Tg and LER effects connected?