Dynamics of Chemical Intermediates in CARs of Post-optical Lithographies

1 μC/cm² 75 keV EB (ca. 0.3 mJ/cm² EUV)

Exposure dose

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   LER dependence on dose, quencher, and line width
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4. Summary
Background of the research at Osaka Univ.

Acid formation mechanism studied by ns-pulse radiolysis and product analysis
- Kozawa et al., JJAP (1992), JVSTB (1997)
- Tagawa et al., SPIE (2000)

Spatial distribution of charges measured by ps-pulse radiolysis
- Saeki et al., JJAP (2002)
- Okamoto et al., CL (2003)

Initial spatial distribution of protons and counter-anions

Acid yield measurement
- Yamamoto et al., JJAP (2004)
- Shigaki et al., JJAP (2006)
- Yamamoto et al., JJAP (2007)
- Hirose et al., JJAP (2007)

Investigation on dynamics of chemical intermediates (proton and acid) in CARs of next-generation lithography by a Monte Carlo simulation
Acid generation mechanism

**Direct excitation**

(In some case, electron transfer from excited polymer)

\[
CA \xrightarrow{h\nu} CA^* \\
CA: \text{PAG (eg. Cation, Anion)}
\]

**Random energy deposition**

\[
M \xrightarrow{h\nu} M^+ + e^- \quad M: \text{Polymer} \\
e^- \xrightarrow{e^-_{\text{th}}} : \text{thermalization} \\
e^{-}_{\text{th}} + CA \rightarrow C^- + A^-
\]

The difference is critical for resist pattern formation, process simulation, and material design.
### Polymer structure dependence of acid yield

<table>
<thead>
<tr>
<th>Polymer</th>
<th>PS</th>
<th>PHS</th>
<th>PαMS</th>
<th>P4MS</th>
<th>PCIS</th>
<th>PBrS</th>
<th>PIS</th>
<th>PtBS</th>
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<tr>
<td>Structure</td>
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<td><img src="image" alt="PHS" /></td>
<td><img src="image" alt="PαMS" /></td>
<td><img src="image" alt="P4MS" /></td>
<td><img src="image" alt="PCIS" /></td>
<td><img src="image" alt="PBrS" /></td>
<td><img src="image" alt="PIS" /></td>
<td><img src="image" alt="PtBS" /></td>
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<table>
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<tr>
<th>Acid generator</th>
<th>Relative acid yield</th>
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<td>TPS-tf</td>
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<table>
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<tr>
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<th>EUV (%)</th>
<th>EB (%)</th>
</tr>
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<tbody>
<tr>
<td>PHS</td>
<td>100.0</td>
<td>100.0</td>
</tr>
<tr>
<td>PBrS</td>
<td>40.4</td>
<td>45.4</td>
</tr>
<tr>
<td>PIS</td>
<td>14.2</td>
<td></td>
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<tr>
<td>P4MS</td>
<td>7.9</td>
<td>12.6</td>
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<tr>
<td>PαMS</td>
<td>2.0</td>
<td>7.1</td>
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<tr>
<td>PtBS</td>
<td>6.5</td>
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<tr>
<td>PS</td>
<td>5.3</td>
<td>5.5</td>
</tr>
</tbody>
</table>

**EUV is categorized into ionizing radiations such as EB**

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**1. Introduction**

Yamamoto et al., JJAP 46 (2007) L142
Chemical reactions in CARs

LER (Line edge roughness)  
= 3 σ (σ: standard deviation)

LWR (Line width roughness)  
= 3 σ

\[
\text{ROH} \cdots \text{ROH}^+ + e^- \quad (1) \text{Ionization}
\]
\[
\text{ROH}^+ + e^- \rightarrow \text{ROH}^* \quad (2) \text{Recombination}
\]
\[
e^- + \text{C}^+\text{A}^- \rightarrow \text{C}^- + \text{A}^- \quad (3) \text{Reaction with PAG}
\]
\[
\text{ROH}^+ + \text{nROH} \rightarrow \text{RO}^- + \text{H}^+(\text{ROH})_n \quad (4) \text{Deprotonation}
\]
\[
\text{H}^+ + \text{A}^- \rightarrow \text{H}^+\text{A}^- \quad (5) \text{Acid formation}
\]
\[
\text{ROR}' \xrightarrow{\text{H}^+} \text{ROH} + \text{X} \quad (6) \text{Deprotection}
\]
\[
\text{ROR}' \xrightarrow{\Delta \text{H}^+\text{A}^-} \text{ROH} + \text{X} \quad (7) \text{Deprotection}
\]
\[
\text{ROH}^* \rightarrow \text{ROH} \quad (8) \text{Deactivation}
\]
\[
\text{H}^+ + \text{Q} \rightarrow \text{Q}(+\text{H}^+) \quad (9) \text{Proton quench}
\]
\[
\text{H}^+\text{A}^- + \text{Q} \rightarrow \text{Q}(+\text{H}^+) + \text{A}^- \quad (10) \text{Acid quench}
\]

The simulation takes into consideration all of the above reactions including the spatial information of each chemical intermediate.
Initial spatial distribution of positive/negative charges

EB: 75 keV (1 nm $\sigma$), trajectories simulated by Sigma-C
Resist: poly(4-hydroxystyrene), PHS $\varepsilon$=4
  PAG: 10 wt% triphenylsulfonium-triflate
  Amine: Mn=400, Concentration: 0.04 –5 wt%
Mesh: 1 nm cubic

$\Delta d = \sqrt{D \Delta t} n + \frac{eD}{k_B T} E \Delta t$

Formation of acid ($H^+A^-$)

Formation of counter-anion

$e^- + C^+A^- \rightarrow C^- + A^-$

Proton-electron distribution (Ave: 4 nm)

Proton-counter-anion distribution
  (Ave: 5.6 nm)

Figure. Initial spatial distribution
Formation process of LER of latent image in CARs

Figure. Latent image formed via catalytic reactions by protons and acids

Time[rc^2/D]
0.0000

Proton dynamics
Green: Proton
Red: Anion
Blue: Acid
2 μC/cm², amine 0.5 wt%
Latent image after acid (H^+A^-) formation before PEB

3. Results and discussion
Kinetic traces of acid formation

\[ \text{H}^+ + \text{A}^- \rightarrow \text{H}^+\text{A}^- \]

Increase of formation time with exposure dose

Effect of 2\textsuperscript{nd}-order reaction

Increase of charge (H\textsuperscript{+}, A\textsuperscript{-}) concentration accelerates the recombination (acid formation) process
3. Results and discussion

Latent image after PEB

- Acid survival probability
- PEB time (10^{-16}/D unit)

Amine concentration (relative to proton-anion pair)

1 µC/cm² 2 µC/cm² 5 µC/cm²

Exposure dose

- 1 µC/cm²
- 2 µC/cm²
- 5 µC/cm²
Time-evolution of catalytic reactions during PEB

**Figure.** Percentage of the catalyzed meshes of 1x100x100 nm cuboid. 5 μC/cm²
3. Results and discussion

Correlation between LER and line width (acid diffusion length)

Exposure dose, quencher → LER decrease

Acid diffusion length → LER decrease and increase

Figure. Latent images of the minimum LER points (amine=0.4).
Contrast curve of latent image

Relative amine conc: const (0.4)

Amine conc: const (0.5 wt%)

Left fig.: Contrast curves are sharpened with exposure dose
Right fig.: Contrast curves are not sharpened so much

Simultaneous increase of dose and quencher enhances the contrast curve

(Capacity of high concentration quencher)
Dependence of LER on exposure dose

**Figure.** LER dependence on exposure dose. The values in brackets represent relative amine conc.

\[ \text{LER} = \alpha \cdot \left( \frac{4100 \rho c}{MD} \right)^\beta \cdot D^\gamma \]

- \( \alpha, \beta, \gamma \): Fitting parameters
- \( \rho \): Resist density
- \( M \): Quencher molecular weight
- \( c \): Quencher concentration
- \( D \): Exposure dose

**Requirement of 1.2 nm LER @ ca. 5 \( \mu \text{C/cm}^2 \)

LER of latent image: ca. 9.5 nm @ 5\( \mu \text{C/cm}^2 \)

(Overestimated, because activation energy and development process are not incorporated. Projection of all catalyzed area on xy plane.)

**Figure.** Correlation between shot noise and LER

Shot noise is ca. 10 % of LER of latent image
Summary

On the basis of ps PR studies, dynamics of protons and acids in CARs of POL were investigated by Monte Carlo simulation.

Relationship between LER (high freq.) of latent images and line width was demonstrated with the parameters of exposure dose, quencher conc, and line width.

The LERs (ca. 9.5 nm @ 5 \( \mu \text{C/cm}^2 \)) are overestimated in comparison to actual observations, because e.g. activation energy and development process are NOT incorporated.

Future works

- Activation energy? Development process?
  
  at next SPIE 2008

- Low frequency LER?
  Formation mechanism etc

- Polymer effects?
  Polymer size, configuration, etc

- EUV ? Smaller line?

- Apply to actual experiments
  Various conditions....
  What happens in real resist system, what limits CAR performance?, how improve LER?
Geminate ion recombination process

Smoluchowski equation

\[ \frac{\partial w}{\partial t} = D \nabla \left( \nabla w + w \frac{1}{k_B T} \nabla V \right) \]

- \(w\): Probability density of pairs
- \(k_B\): Boltzmann constant
- \(V\): Coulomb potential
- \(T\): Absolute temperature
- \(D\): Sum of diffusion coefficient

Initial distribution function

\[ f(r, r_0) = \frac{1}{r_0} \exp\left(-\frac{r}{r_0}\right) \]

- \(r\): Distance between radical cation and electron
- \(r_0\): Initial separation distance on average

RH \(\rightarrow\) RH\(^+\)\(\cdot\) + e\(^-\)
RH\(^+\)\(\cdot\) + e\(^-\) \(\rightarrow\) RH\(^*\)
Kinetic decay of cation radical of n-dodecane obtained in the subpicosecond pulse radiolysis of neat n-dodecane, monitored at 790 nm.

**Time Profile of Radical Cation**

\[ C_{12}H_{26}^+ + e^- \rightarrow C_{12}H_{26}^* \]

**Distribution of Electron**

- \( r_0 = 6.6 \) nm
- \( D = 6.4 \times 10^{-4} \text{cm}^2/\text{s} \)
- \( \varepsilon = 2.012 \)
Incorporation of polymer effect. Example of solution study

Intermolecular interaction (L-J, Coulomb)
Intra-molecular interaction (bend, torsion)

Configure molecules at the lowest energy position including fluctuation of thermal energy.

Average energy required to produce an ion pair (W-value)

Fig. 3. Photon W-value for Ar as a function of photon energy. The solid circles show the present result, and the open squares are the data of Combecher for electrons. The solid curve represents the photon W-values calculated by the model here. The arrow indicates the 2p ionization threshold. [N. Saito, I. H. Suzuki, Radiat. Phys. Chem. 60 (2001) 291.]

W-value = \frac{100 \ (eV)}{G-value}

Ionization energy (Ar): 15.759, 15.937 eV

K-edge
Carbon: 284 eV
Oxygen: 547 eV

W-value in PHS
22.2 eV (75 keV EB)
Correlation between LER and line width (acid diffusion length)
Correlation between LER and line width (acid diffusion length)
LER, LWR

**LER (Line edge roughness)**

\[
LER = 3 \times \sqrt{\frac{\sum_{i=1}^{n} (x_i - x_{\text{ave}})^2}{n}}
\]

**LWR (Line width roughness)**

\[
LWR = 3 \times \sqrt{\frac{\sum_{i=1}^{n} (x_i - x_{\text{ave}})^2}{n}}
\]

If there is no correlation of roughness between left and right.

\[
LWR = \sqrt{\text{LER}_{\text{right}}^2 + \text{LER}_{\text{left}}^2} = \sqrt{2} \times \text{LER}
\]