Time Resolved Spectroscopy of Nanoparticle EUV Photoresists

Reactions of HfO nanoparticles with electrons and the following solubility change studied by pulse radiolysis

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Nanosecond Pulse Radiolysis System

**Pulse radiolysis system**

**LINAC (L-band electron linear accelerator)**
- 28 MeV 8 ns

**Wavelength Range**
- 300 nm ~ 2500 nm
- 200 Gy / pulse

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Results

Pulse radiolysis studies on solvated electrons in methanol

\[ \text{CH}_3\text{OH} \rightarrow \text{CH}_3\text{OH}^+ + e_s^- \]

\[ \text{CH}_3\text{OH} + \text{CH}_3\text{OH}^+ \rightarrow \cdot \text{CH}_2\text{OH} + \text{CH}_3\text{OH}_2^+ \]

\[ \text{CH}_3\text{OH}_2^+ + e_s^- \rightarrow \text{Neutral Products} \]

Additive + e_s^- \rightarrow \text{Products}

HfO nanoparticle (HfO2MA4) was given by Chris Ober.

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The rate constant of acid generators with solvated electrons in methanol

Fig. Time dependent behavior of solvated electrons obtained by the pulse radiolysis of diphenyliodonium triflate solutions in methanol, monitored at 650 nm.

<table>
<thead>
<tr>
<th>Ionic Acid Generator</th>
<th>Rate Constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>DPI-CF₃SO₃</td>
<td>2.4 × 10¹⁰ M⁻¹ s⁻¹</td>
</tr>
<tr>
<td>TPS-CF₃SO₃</td>
<td>2.7 × 10¹⁰ M⁻¹ s⁻¹</td>
</tr>
<tr>
<td>TPS-SbF₆</td>
<td>2.5 × 10¹⁰ M⁻¹ s⁻¹</td>
</tr>
<tr>
<td>CMS-CF₃SO₃</td>
<td>1.6 × 10¹⁰ M⁻¹ s⁻¹</td>
</tr>
<tr>
<td>NAT-CF₃SO₃</td>
<td>1.9 × 10¹⁰ M⁻¹ s⁻¹</td>
</tr>
</tbody>
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<table>
<thead>
<tr>
<th>Non-ionic Acid Generator</th>
<th>Rate Constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>TAZ</td>
<td>2.2 × 10¹⁰ M⁻¹ s⁻¹</td>
</tr>
<tr>
<td>TAZ 2</td>
<td>2.5 × 10¹⁰ M⁻¹ s⁻¹</td>
</tr>
<tr>
<td>DNB</td>
<td>2.2 × 10¹⁰ M⁻¹ s⁻¹</td>
</tr>
<tr>
<td>DS</td>
<td>1.1 × 10¹⁰ M⁻¹ s⁻¹</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Base Polymer</th>
<th>Rate Constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>m-cresol novolac</td>
<td>10⁷ ~ 10⁸ baseM⁻¹ s⁻¹</td>
</tr>
</tbody>
</table>

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HfO nanoparticle (HfO2MA₄) pulse radiolysis Spectra

[Condition]
- Concentration: Left figure: MeOH  Right figure: 2.5mM Hf nano particle in MeOH
  Ar Bubbling (10min.)  Wavelength  350nm-800nm

MeOH

2.5mM Hf nano particle in MeOH

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Hf nano particle pulse radiolysis result @ 640nm

[Condition]
- Concentration: Left figure: MeOH  Right figure: 2.5mM Hf nano particle in MeOH
- Ar Bubbling (10min.)
- Wavelength 640nm

Hf nano particle in MeOH

\[ e^- + \text{Hf nano particle} \rightarrow \text{Hf nano particle} \cdot^- \]

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**Hf nano particle pulse radiolysis result @ 1340nm**

[Condition]
- Concentration: Left figure: CH₃CN  Right figure: 2.5mM Hf nano particle in CH₃CN  
  Ar Bubbling (10min.)
- Wavelength 1340nm

\[
\text{Hf nano particle in CH}_3\text{CN} \\
(e^-, \text{CH}_3\text{CN}^-, (\text{CH}_3\text{CN})_2^-) + \text{Hf nano particle} \rightarrow \text{Hf nano particle}^-
\]

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**Example**
TPS-Tf in CH3CN; \(6.3 \times 10^{10} \text{[M}^{-1} \cdot \text{s}^{-1}]\)
Pulse Radiolysis Results

- HfO nanoparticles react with solvated electrons in CH$_3$OH and CH$_3$CN very effectively.
- The rate constant of HfO nanoparticles with solvated electrons in CH$_3$CN is $1.4 \times 10^{10}$M$^{-1}$s$^{-1}$.
- During pulse irradiation of HfO nanoparticles in THF and CH$_3$CN, aggregation occurs.
Dynamic light scattering measurements of HfO aggregated particle produced in irradiated solutions
Dynamic light scattering measurement of HfO aggregated particle

Zetasizer

Measurement conditions

Room temperature 24 °C
1.2×1.2cm² crystal cell
Cell Length 10mm
Dynamic light scattering

Using Zetasizer (Sysmec)

HfO in 5mM acetonitrile after pulsed electron irradiation

Peak 1

Peak 2

<table>
<thead>
<tr>
<th></th>
<th>Diam. (nm)</th>
<th>% Intensity</th>
<th>Width (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peak 1:</td>
<td>2185</td>
<td>96.0</td>
<td>26.75</td>
</tr>
<tr>
<td>Peak 2:</td>
<td>0.000</td>
<td>4.0</td>
<td>471.3</td>
</tr>
<tr>
<td>Peak 3:</td>
<td>0.000</td>
<td>0.0</td>
<td>0.000</td>
</tr>
</tbody>
</table>

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Aggregated HfO nanoparticle after pulsed EB irradiation (pulse radiolysis measurement) were observed by dynamic light scattering method (Zetasizer: Sysmecs) However, in the case of irradiated THF solution, we could not measured because the aggregated particles was precipitating. On the other hand, for acetonitrile solution, although a low concentrated one (5mM HfO) was measured, high concentrated one (20mM HfO) could not be measured.

SEM measurements of HfO aggregated particle produced in irradiated solutions were carried out. Sample preparation of observation HfO solution was spin-coated the Si wafer. Spin condition: 2500rpm 30s. After spin-coating and SEM measurement was carried out.

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Non irrad. 5mM in THF

Irrad. 5mM in THF

Irrad. 25mM in THF

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Results of Particles Size Measurement

Size of aggregated HfO nano particle after pulsed EB irradiation were evaluated.

In irradiated THF solution, particle size showed about 300nm - 450nm (Rough value).

In irradiated acetonitrile solution, particle size showed about 100nm -500nm.

Particle size increased with concentration.
Conclusion

• HfO nanoparticles react with solvated electrons in CH₃OH and CH₃CN very effectively.
• The rate constant of HfO nanoparticles with solvated electrons in CH₃CN is 1.4 x 10¹⁰M⁻¹s⁻¹.
• During pulse irradiation of HfO nanoparticles in THF and CH₃CN, aggregation occurs.
• Dynamic light scattering and SEM measurements of HfO aggregated particle produced in irradiated solutions.

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