Sensitization and reaction mechanisms of ZrO$_2$ nanoparticle resist used for extreme ultraviolet lithography

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Lithography roadmap

<table>
<thead>
<tr>
<th>Year</th>
<th>2001</th>
<th>04</th>
<th>07</th>
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<th>19</th>
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<th>25</th>
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<tbody>
<tr>
<td>Line width (nm)</td>
<td>130</td>
<td>90</td>
<td>65</td>
<td>45</td>
<td>28</td>
<td>22</td>
<td>17</td>
<td>13</td>
<td>10</td>
<td>7.7</td>
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<tr>
<td>LWR (nm)</td>
<td>2.4</td>
<td>1.8</td>
<td>1.4</td>
<td>1.1</td>
<td>0.8</td>
<td>0.6</td>
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<tr>
<td>Lithography solutions</td>
<td>KrF 248nm</td>
<td>ArF 193nm</td>
<td>ArF immersion (+DP) 193nm</td>
<td>EUV 13.5nm</td>
<td>EB for mask production</td>
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Two keywords in the development of resist materials and processes

Transition of basic science for material design

Trade-off relationships between resolution, LWR, and sensitivity

Resolution

LWR(LER)

Sensitivity

Radiation chemistry

Ionization energy (~10eV)

Photochemistry

Energy (eV)

Line width (nm)

LWR (nm)

Exposure tool
Strategy for development of resist materials

- Time-resolved spectroscopy
- Nanopatterning

Electron linear accelerator
- Ultrashort electron beam
- Time resolution <1 ps
- Survey of elementary reactions
- Integration of elementary reactions

EUV lithography system
- High-quality optical image
- Spatial resolution <20 nm
- Analysis of SEM images
- Resolution, LER/LWR, Sensitivity

Modeling

Server
- Inverse analysis

1000 cores

Patterning information

Inverse analysis

Elucidation of reaction mechanism in real materials and extraction of resist parameters

Material design

Acceleration of development cycle
Pattern formation in metal oxide nanoparticle resist

Nanoparticle: ZrO$_2$
Ligand: Methacrylic acid (MAA)

NP
- W-value
- Band gap
- Density
- Absorption coefficient
- Particle size (volume)
- IMFP
- Redox potential
- Hole mobility
- Electron mobility
- Concentration

Ligand shell
- W-value
- Ionization energy
- Density
- Inelastic mean free path (IMFP)
- Absorption coefficient
- Thermalization distance
- Chemical reactions
- Concentration

Number of electron-hole pairs generated in ZrO$_2$ core and ligand shell

Fig. Distribution of sum of the numbers of electron-hole pairs in zirconia core and the closest MAA shell (ZrO\(_2\) ratio 0.5).
Threshold for insolubilization (ZrO$_2$ ratio 0.5)

Fig. Dependence of line width on exposure dose and half-pitch.

Average at boundary between lines and spaces: 1.77 electron-hole pairs

Threshold for insolubilization

Both electron and hole availabilities are unknown.
LER is considered to be inversely proportional to the chemical gradient (dN/dx) in the right chemical system.

Chemical system (reaction mechanism) has not been optimized.
The number of electron-hole pairs generated upon exposure to 1 mJ cm$^{-2}$ EUV radiation

In a ZrO$_2$ core : 0.16
In a ligand shell : 0.04-0.17

The efficient use of electrons and holes are essential to the design of chemical system.
Pulse radiolysis for study of elementary reactions

1. Generation of electron-hole pairs in well-studied matrix A (H\textsubscript{2}O or CH\textsubscript{2}Cl\textsubscript{2})

   - **Ultrashort EB pulse**
   - **Well-studied matrix A**
   - **Electron linear accelerator**

   \[
   \begin{align*}
   \text{H}_2\text{O} & \xrightarrow{\text{\color{red}{\textbullet}}} \text{H}_2\text{O}^+ + \text{e}^- \\
   \text{H}_2\text{O}^+ + \text{H}_2\text{O} & \rightarrow \text{H}_3\text{O}^+ + \text{OH}^- \\
   \text{B} + \text{e}^- & \rightarrow \text{B}^- \\
   \end{align*}
   \]

2. Study of reaction of electron-hole pairs with target molecules B (MAA)

   - **Reaction of electrons**
     - \[\text{H}_2\text{O} \xrightarrow{\text{\color{red}{\textbullet}}} \text{H}_2\text{O}^+ + \text{e}^-\]
     - \[\text{H}_2\text{O}^+ + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{OH}^-\]
     - \[\text{B} + \text{e}^- \rightarrow \text{B}^-\]

   - **Reaction of holes**
     - \[\text{CH}_2\text{Cl}_2 \xrightarrow{\text{\color{red}{\textbullet}}} \text{CH}_2\text{Cl}_2^+ + \text{e}^-\]
     - \[\text{CH}_2\text{Cl}_2 + \text{e}^- \rightarrow \text{CH}_2\text{Cl}^- + \text{Cl}^-\]
     - \[\text{B} + \text{CH}_2\text{Cl}_2^+ \rightarrow \text{B}^+ + \text{CH}_2\text{Cl}_2\]

3. Detection and tracking of intermediates (e\textsuperscript{-}, B\textsuperscript{-}, or B\textsuperscript{+})

   - **Ultrashort EB pulse**
   - **Time-resolved spectroscopy with white analyzing light**
   - **White light**

   \[
   \begin{align*}
   \text{Elimination of reactive hole species} \\
   \text{Elimination of electrons}
   \end{align*}
   \]
Reaction of ligands with electrons

Fig. Kinetic trace of hydrated electrons obtained in the pulse radiolysis MAA solution in water.

Fig. Kinetic trace of hydrated electrons obtained in the pulse radiolysis IBA solution in water.

Rate constant for the reaction with hydrated electrons

\[ B + e^- \rightarrow B^- \]

MAA: \( 1.59 \times 10^{10} \text{ M}^{-1}\text{s}^{-1} \)

IBA: \( 1.37 \times 10^9 \text{ M}^{-1}\text{s}^{-1} \)
Decomposition of MAA anion radicals

Fig. Transient absorption spectra obtained in the pulse radiolysis of MAA solution in water at 400 ns after an electron pulse.

Fig. Transient absorption spectra obtained in the pulse radiolysis of IBA solution in water at 400 ns after an electron pulse.

\[
\text{MAA} \quad \alpha\text{-carbon radical}
\]

\[
\text{IBA}
\]

Optical density (arb. unit)

Wavelength (nm)

Time (ns)

Optical density (arb. unit)

-100 0 100 200 300 400

300 400 500 600 700 800 900

0 0.02 0.04 0.06 0.08 0.1 0.12

0 0.05 0.1 0.15 0.2

0 0.05 0.1 0.15 0.2

\[
\text{\textit{a}-carbon radical}
\]

Radical recombination ?

Radical addition ?

\[
\text{\textit{a}-carbon radical}
\]
Fig. Kinetic traces of intermediates obtained in the pulse radiolysis 0.1 M MAA solution in CH₂Cl₂ with 0, 0.1, and 1M ethanol, monitored at 540 nm.
Possible reactions in real chemical system

\[
\text{O} \quad \text{OH} \quad .+ \quad \text{O} \quad \text{OH} \quad .+ \quad \text{e}^- \quad (\text{including oxidation on ZrO}_2 \text{ core surface})
\]

\[
\text{O} \quad \text{OH} \quad .+ \quad \text{e}^- \rightarrow \text{O} \quad \text{OH} \quad \text{(including reduction on ZrO}_2 \text{ core surface})
\]

\[
\text{O} \quad \text{OH} \quad + \text{H}^+ \rightarrow \text{O} \quad \text{OH} \quad \text{Radical recombination?}
\]

\[
\text{O} \quad \text{OH} \quad .+ \quad \text{e}^- \rightarrow \text{O} \quad \text{OH} \quad \text{Radical addition?}
\]
Effect of acid generator on chemical system

- Suppression of MAA anion radical yield
- Increase of MAA cation radical yield through the suppression of ion recombination
- Suppression of electron migration
- Generation of anions

\[
\begin{align*}
\ce{=C(\cdot\cdot)O-H} & \rightarrow \ce{=C(\cdot\cdot)O-H}^+ + e^- \\
\ce{\text{(including oxidation on NP surface)}} \\
\ce{\text{AG Trap}} \\
\ce{\text{(including reduction on NP surface)}} \\
\ce{\text{Suppression of reduction on NP surface}} \\
\ce{\text{Generation of anions}}
\end{align*}
\]
Effect of acid generator on resist pattern

1:5 L&S pattern
120 nm pitch
Developer: $n$-BA

- Suppression of MAA anion radical yield
- Increase of MAA cation radical yield
- Suppression of electron migration
- Balanced out

Both electron and hole contribute to pattern formation.
Summary

○ The radiation chemistry of ligands (MAA) was investigated using a pulse radiolysis method.
○ Both electrons and holes generated upon EUV exposure result in MAA radicals.
○ Both the reaction paths through MAA cation radicals and anion radicals are considered to lead to the insolubilization of the resist.
○ The acid generators suppressed LWR probably through capturing the thermalized electrons.

Acknowledgement

This work was partially supported by Ministry of Economy, Trade and Industry (METI) and the New Energy and Industrial Technology Development Organization (NEDO).