Recent Progress in Nano-space Radiation Chemistry
Research on Sensitivity Enhancements of EUV Resists

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Contents

• Last year, I explained two important things in RLS trade-off problem.
  (1) The origin of RLS trade-off problem and how to solve RLS trade-off problem.
  (2) The importance of nanospace radiation chemistry in solving the RLS trade-off problem.
• The present paper shows 3 important topics of the importance of detailed nano-space radiation chemistry in sensitivity enhancements of chemically amplified EUV resists.
  (1) Fluorinated polymer resists (High Energy Absorption)
  (2) Acid amplified resists (High Yield Acids)
  (3) EUV resists at 6.x nm (Future Problem)
Most researchers had arrived at the RLS trade-off triangle.


Simulations: G.M. Gallatin, Proc. SPIE (2005) (Simulations does not contain EUV-induced acid generation mechanism and no fundamental differences in simulations among ArF, EB and EUV resists after latent acid image formation.)
Resist Pattern Formation Processes of EUV Resists

- Exposure (Tool)
- Interaction of EUV with resists (Topics 1, Topics 2, Topics 3)
- Acrylic acid generation (Topics 1, Topic 2)
- Acid diffusion and deprotection reaction
- Acid catalyzed image (Latent image after PEB)
- Development

Nanospace radiation chemistry in EUV resists.

Acid generation processes are very important in solving RLS trade-off problem.

Budget (Acid yield and acid profile)

How to use budget for RLS trade off.

RLS Trade-Off Exists.
EUV Mechanism\(^1\) Provides RLS Gain?

\(^1\)Kozawa, et al. JVSTB 25, 2481 (2007)

- Resist Sensitivity Improved 30-50% via Addition of EUV Sensitizing Agents
- No Loss In Resolution, No Degradation in LWR

\(\textbf{Multiple Suppliers Achieving Similar Results in 1H’08}\)

Reported by Todd R. Younkin (Intel Corporation) in Litho Forum 2008
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Interaction of EUV photon with CARs

Lambert’s law

Intensity of EUV ($I$)

$$\frac{\partial I}{\partial z} = -\alpha I$$

Absorption coefficient ($\alpha$)

PHS : 3.8 $\mu$m$^{-1}$

Topics (1) Pulse radiolysis research on the detailed mechanisms of acid generation of chemically amplified EUV fluorinated polymer resists

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Absorption enhancement of incident energy

How to increase resist absorption

\[ c(z) = \phi \left( \frac{-dI}{dz} \right) = \phi \alpha I_0 e^{-\alpha z} \]

- \( c \): acid concentration
- \( \phi \): acid generation efficiency
- \( \alpha \): absorption coefficient
- \( I \): light intensity
- \( z \): distance from the surface in depth direction

Fluorination of polymer

[H. Yamamoto et al. APEX 1 (2008) 047001.]

Fig. Depth profile of acid concentration (the number of molecules per unit volume) calculated with acid generation efficiency, absorption coefficient, and the exposure dose of 5 mJ/cm².
Understanding of acid generation mechanisms and synthesizing new chemical structures of fluorinated polymer resists are important in enhancement of acid generation.

General: Ultra thin resists, increase in PAG concentrations, etc.

Subpicosecond Pulse Radiolysis System

Femtosecond Electron Linear Accelerator

- Master oscillator
- E-gun
- Linac control panel
- L-band linac
- Magnetic pulse compression
- SHPB amplifier
- Klystron

Pump & Probe Spectroscopy

- Time jitter compensation
- Light detection system
- Optical delay

To other devices such as oscilloscope and so on.

Femtosecond laser system

- Femtosecond laser
- Pulse generator
- Trigger generator with synch. circuit
- GPIB

Other devices include:
- Oscilloscope
- Other related equipment
Clarification of Electron Flow in Chemically Amplified Resist

EUV

\[ PF^+ \]

Fluorinated polymer

Ionization

Recombination

\[ e^- \]

Decomposition of acid generator (RX)

Dissociation

\[ RX \rightarrow X^- \]

Electron attachment

Radical anion formation

\[ PF \]

\[ p_1 \]

Electron transfer

\[ p_2 \]

Dissociation

\[ F^- \]

\[ Rx \]

Virtual effective reaction radius, \( R_p \)

\[ R_p = p_2 R_{PF} \]
Both acid generation efficiency $\phi$ and absorption coefficient $\alpha$ of 8FN are larger than those of 1FN.
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The high sensitivity of EUV resists is strongly required. Acid amplification produces high content of strong acids in a nanospace.
The Acid Production Pathway

PHS $\xrightarrow{EUV}$ PHS$^{\bullet+}$ + e$^-$

Deprotonation

TPS-Tf$^*$

H$^+$ $\rightarrow$ TfOH

TPS-Tf

Electron Transfer

PiXX$^-$

(XX = Ts, 1F, 3F)

H$^+$ $\rightarrow$ DEA Recombination $\rightarrow$ Acid

PiTs decreases acid yield, but Pi3F increases acid yield.

PiTs decreases acid yield, but Pi3F increases acid yield.
The long-lived Pi3F•− radical anions efficiently undergoes the electron transfer to TPS-Tf to form TPS-Tf•−, which then decomposes to generate TfOH.

Good acid amplifiers are quite important in increasing acid generation.
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Extendibility of EUV resists in the exposure wavelength from 13.5 down to 3.1 nm for next-generation lithography

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Experimental Results on Resist Sensitivities

Obtained sensitivities ($E_0$) of the resist materials for each EUV/soft X-ray source.

<table>
<thead>
<tr>
<th>Wavelength [nm]</th>
<th>TDUR-P722</th>
<th>$E_0$ [mJ/cm²]</th>
<th>ZEP520A</th>
<th>ZEP7000</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.1</td>
<td>2.5</td>
<td>11</td>
<td>1.0</td>
<td></td>
</tr>
<tr>
<td>3.9</td>
<td>1.9</td>
<td>9.0</td>
<td>0.60</td>
<td></td>
</tr>
<tr>
<td>5.0</td>
<td>9.6</td>
<td>17</td>
<td>1.4</td>
<td></td>
</tr>
</tbody>
</table>

Conclusion: 1. Absorbed doses (Gy: Gray, J/kg) are almost constant for each resist.
2. $E_0$ (mJ/cm²) is scattered and determined by linear absorption coefficients.
Photoabsorption Crosssection at 6.7 nm and 13.5 nm

Linear absorption coefficient = Density x Photoabsorption cross section
1. Each resist material would have its particular value of the absorbed dose (Gray: J/kg) for pattern formation, regardless of the exposure wavelengths in the range of EUV/soft X-rays from 13.5 to 3.1 nm. In other words, this result suggested that the linear absorption coefficient would be the major factor for determination of the exposure wavelength dependence of resist sensitivity (mJ/cm²), although there are other minor important factors such as energies of the secondary electrons, that is, thermalization length and initial configuration of reactive intermediates (multi-spur effects).

2. If resist sensitivity to a certain wavelength is obtained, the sensitivities to other wavelengths could be roughly estimated with respective linear absorption coefficients in the range of EUV/soft X-rays. At 6.7 nm exposure, resists containing S, P, and Si atoms have large linear absorption coefficients.

<table>
<thead>
<tr>
<th>Wavelength [nm]</th>
<th>PHS</th>
<th>ZEP</th>
<th>S</th>
<th>a-Si</th>
<th>HSQ</th>
<th>PSQ</th>
<th>PMPS</th>
</tr>
</thead>
<tbody>
<tr>
<td>13.5</td>
<td>3.7</td>
<td>4.6</td>
<td>2.0</td>
<td>1.4</td>
<td>4.4</td>
<td>4.2</td>
<td>6.5</td>
</tr>
<tr>
<td>6.7</td>
<td>0.83</td>
<td>1.1</td>
<td>19</td>
<td>18</td>
<td>6.5</td>
<td>3.6</td>
<td>5.5</td>
</tr>
</tbody>
</table>

hydrogen silsesquioxane, (HSQ, 1.4 g cm⁻³), poly(2-methyl-1-pentenesulfone) (PMPS, 2.2 g cm⁻³)
The improvement at each stage is required cloth to its physical and chemical limit. The good integration of improvement at each stage is strongly needed for the development of next generation EUV resists. Especially understanding nanospace radiation chemistry is important and essential in the development of high performance EUV resists.
THANK YOU FOR YOUR KIND ATTENTION.