Status and Challenge of Chemically Amplified Resists for Extreme Ultraviolet Lithography

1. Status and challenge
2. Anion-bound resist
3. Wavelength diffusion

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Two keywords in the development of resist materials and processes:

- Trade-off relationships between resolution, sensitivity, and LER
- Ionization energy (~10eV)
Chemically amplified resist

Typical components: Polymer, Acid generator, Quencher

Role: Conversion of energy modulation to binary image

Exposure source
Energy modulation of quantum beam

SEM image of resist

Resist image

Energy deposition
Photon/electron interaction with matter

Formation of acid image
Energy deposition

Thermal energy
Formation of acid image

Decomposition of acid generator
Thermal energy

Solubility change through chemical reaction
Formation of latent image

Acid diffusion, deprotection
Development

Dissolution of molecules
Development
**Relationship between LER and chemical gradient**

- **EUV**
- **Acid Image**
- **Latent Image**
- **Pattern**

- **Mixture of soluble and insoluble molecules**
  - Absolutely stochastic
  - Can not be controlled

- **(Spatially) partially soluble**

- **LER formation**

- **LER \(\propto\) width of intermediate region \(\approx\) \(\frac{1}{\text{Chemical gradient}}\)

- **LER \(\approx\) \(\frac{f_{LER}}{dm / dx}\)**
IMEC, Sematech, and Selete (EIDEC) have supported the development of EUV lithography including resist material and processes. A large number of resist materials have been tested in these sites.

Evaluation of resist performance is tricky because of the trade-off relationship.
Performance (efficiency) of resist

The number of incident photons is limited because of the sensitivity requirement.

① How many photons can be absorbed?

Absorption coefficient: \( \sim 4 / \mu \text{m} \)

② How many acids can be generated by a single photon?

Quantum efficiency: 2-3

③ How many dissolution inhibitor (protecting group) can be removed by a single acid during the diffusion of unit length?

Effective reaction radius

④ How smoothly are the polymers dissolved in developer?

Relationship between LER and chemical gradient, \( f_{LER} \)

\[
\text{LER} \approx \frac{f_{LER}}{dm/dx} \quad \text{The chemical gradient is determined by ①—③}
\]

Generally, resists are evaluated using resolution, LER, and sensitivity.

We in collaboration with Selete evaluated the effective reaction radius and \( f_{LER} \) to understand the current status of chemically amplified resists.
Small Field Exposure Tool: SFET

<table>
<thead>
<tr>
<th>Items</th>
<th>Target Specifications</th>
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<td>Illumination mode</td>
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Selete has reported highest performance resists among those tested using SFET as

Selete Standard Resists (SSR1 to SSR7)
Representative patterning results

SSR4

24 nmHP, 10 mJ cm\(^{-2}\)

Line width, LER (Top down)

Thickness (0 degree)

SSR5

24 nmHP, 10 mJ cm\(^{-2}\)
26 nmHP, 10 mJ cm\(^{-2}\)
32 nmHP, 10 mJ cm\(^{-2}\)
32 nmHP, 11 mJ cm\(^{-2}\)
32 nmHP, 8 mJ cm\(^{-2}\)
32 nmHP, 12 mJ cm\(^{-2}\)
Exposure dose (mJ cm$^{-2}$)

Deviation from half-pitch (nominal line width) (nm)

LER (nm)

Line width

(a) SSR4

(b) SSR5
Simulation result

**Line width**

Exposure dose (mJ cm\(^{-2}\))

- Deviation from half-pitch (nominal line width) (nm)
- Half-pitch (nm)

**LER**

Exposure dose (mJ cm\(^{-2}\))

- LER (nm)
- Half-pitch (nm)

(a) SSR4

(b) SSR5
Reconstruction of latent images from does-pitch matrices of line width and LER (SSR3)

Bridge

\[ LER = \frac{0.31}{dm/ dx} \]

Chemical gradient

Dissolution point

Dissolution rate 2.4 nm s\(^{-1}\)

Line width, LER

Normalized protected unit concentration

Distance (nm)

Normalized protected unit concentration

Distance (nm)
## Evaluated parameters

<table>
<thead>
<tr>
<th>Resist</th>
<th>Matrix</th>
<th>Effective reaction radius (nm)</th>
<th>$f_{LER}$</th>
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<td>Polymer</td>
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<td>Polymer</td>
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<td>SSR7</td>
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**Diagram:**
- **Reaction site**: Proton and anion are shown with a distance of 0.3 nm.
- **Chemical reaction**:
  - $Q$ conc.: 0.02
  - $dC/dx$: 0.48
  - $\delta x$: 5.6
- **LER**:
  - $+0.4\sigma$
  - $-0.4\sigma$
  - Dissolution line

**Graph**: A graph illustrating dissolution line with $dC/dx$, $\delta x$, and $\sigma$.
Challenges

15 nm features has been reported to be resolved with 30 mJ/cm$^2$ sensitivity.

- Half-pitch: 16 nm
- Optical contrast: 0.8
- Eff. reaction radius: 0.1 nm
- $f_{LER}$: 0.2

Absorption coefficient: Sum of absorption cross section of atoms
Quantum efficiency: Acid generator concentration
Effective reaction radius: Activation energies for deprotection and diffusion
Summary (1)

We have investigated resist patterns fabricated using an EUV exposure tool on the basis of reaction mechanisms. To simultaneously meet the requirements of resolution, LER, and sensitivity, it is essential to enhance the absorption coefficient of the resist, the quantum efficiency of acids, and the effective reaction radius of catalytic chain reaction. Especially, the absorption enhancement is the most important factor. Actually, it is not difficult to increase the absorption coefficient of the polymer, because the absorption coefficient against EUV is determined, not by chemical bonds but the photoabsorption cross sections of atomic elements. The problem is that the introduction of new atomic elements to the polymer significantly changes the chemistry induced in the resist films. It is not an easy task to increase the effective reaction radius of chemical reactions in the new resist platform to the same level as that in well-studied organic resist polymers.
Anion bound resist

It has been considered that the acid diffusion is the most serious problem for the improvement of resist performance in terms of trade-off relationship.

Recently, a chemically amplified resist with anion-bound acid generator attracted much attention.

Promising material for 16 nm node and beyond

Reaction mechanism is unknown.

An acid diffusion model in a chemically amplified resist with anion-bound acid generator

New simulation code was developed on the basis of radiation chemistry.

For the development of resist materials, particularly, used in the 16 nm node and beyond, it is important to understand the reaction mechanism of catalytic reactions induced in the anion-bound resists.
Basic idea

Similar sensitivity to that of blend type resists

- The efficiency of acid catalytic reaction is not bad.
- Protons can diffuse. (Experimentally confirmed)
  

High resolution

- Protons cannot diffuse freely.

Protons diffuse under the electric field produced by anions.

Initial distribution

Proton diffusion model

SFET
Annular
18.16 mJ cm$^{-2}$
Representative patterning results

Chemically amplified resist with anion-bound AG

Changing HP

Changing exposure dose

Conventional dose-pitch analysis

Relationship between LER and chemical gradient
Analysis of dose-pitch matrices of anion-bound resist

Exposure dose (mJ cm\(^{-2}\))

- Experimental
- Simulation

Deviation from half-pitch (nominal line width) (nm)

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LER = \frac{0.20}{dm/dx}

m: normalized protected unit concentration
Sensitization mechanism of EUV resists

EUV photon \( h\nu \)

\[ E < E_{th} \]

Thermalization

\[ E > E_{th} \]

Next ionization or excitation

Ionization

Ionization

Proton generation

Acid generator

Anion generation

E \( \rightarrow \) photon

electron

- Resist

\[ E_{th} \]: Threshold energy for electronic excitation

\[ I_e \]: Ionization energy

Simulation processes

1. Absorption
2. Deceleration
3. Deceleration
4. Electron diffusion and reaction

Post exposure baking (PEB)

\[ E = 25 \text{ meV} \]

\[ 25 \text{ meV} < E < E_{th} \]
Immediately after exposure, protons are separated from anions because of their different origins.

Monte Carlo simulation

$$\delta \mathbf{r} = \frac{eDE}{kT} \delta t + \sqrt{6D\delta t} \mathbf{n}$$

Electric field

Displacement of proton

Random vector
Comparison with SFET exposure (22 nm half-pitch)

Dose: 18.16 mJ cm$^{-2}$

PEB time dependence

Quencher concentration dependence
Dose dependence of latent image (26 nm half pitch)

- Dose: 18.16 mJ cm\(^{-2}\)
- Dose: 17.33 mJ cm\(^{-2}\)
- Dose: 18.99 mJ cm\(^{-2}\)
Half-pitch dependence of latent image

Distance (nm)

Protected unit conc. (nm$^{-3}$)

Line  Space  Line

22 nm HP

Distance (nm)

Protected unit conc. (nm$^{-3}$)

Line  Space  Line

23 nm HP

Distance (nm)

Protected unit conc. (nm$^{-3}$)

Line  Space  Line

24 nm HP

Distance (nm)

Protected unit conc. (nm$^{-3}$)

Line  Space  Line

25 nm HP

Pattern boundary (Exp.)

Chemical gradient (Exp.)

Dissolution line

Dose: 18.16 mJ cm$^{-2}$
Summary (2)

The catalytic chain reaction induced in a chemically amplified resist with anion-bound AG was modeled. The calculated latent images were compared with the resist patterns fabricated using SFET of EIDEC. In the preliminary examination, the calculated images well agreed with the experimental results. The detailed analysis of resist patterns using the developed simulation code is ongoing to obtain the material design strategy for 16 nm node and beyond.

Acknowledgement

This work was partially supported by the New Energy and Industrial Technology Development Organization (NEDO).
The electron with thermal energy can sensitize acid generators.

\[ E_{th} \text{: Threshold energy for electronic excitation} \]
\[ I_e \text{: Ionization energy} \]

**Simulation processes**

1. Absorption
2. Deceleration
3. Deceleration
4. Electron diffusion and reaction

\[ E_{th} < E < h\nu - I_e \]
\[ 25 \text{ meV} < E < E_{th} \]
\[ E = 25 \text{ meV} \]
Wavelength dependence of resolution blur caused by secondary electrons

EUV photon

Multiple scattering at $<E_{th}$
Electronic migration after thermalization

Spherically symmetric

Probability density (nm$^{-1}$) $\times$ quantum efficiency

Distance, $\sqrt{x^2 + y^2 + z^2}$ (nm)
Spherical coordinate

Probability density (nm$^{-1}$) $\times$ quantum efficiency

Distance, $x$ (nm)
$x$ coordinate

per unit spherical shell thickness

2 nm
12 nm
13.5 nm

2 nm
13.5 nm
Performance of conventional chemically amplified resists – Resolution -

Acid image resolution (acid diffusion length does not depend on wavelength)

Optical blur, $b_{\text{optical}}$

\[ b_{\text{optical}} = \frac{CD}{2} \quad \text{CD} = k_1 \frac{\lambda}{NA} \]

Secondary electron blur, $b_{\text{electron}}$

Average distance

Total blur, $b_t = \sqrt{b_{\text{optical}}^2 + b_{\text{electron}}^2}$

\[
\begin{align*}
\frac{k_1}{NA} &= 0.5 \\
\frac{k_1}{NA} &= 1
\end{align*}
\]
Performance of conventional chemically amplified resists – Sensitivity

Acid concentration (acid diffusion length does not depend on wavelength)

Absorption coefficient

Acid generation efficiency per unit absorbed dose (G value)

The W-value increases by 10-20% at the absorption edge of the inner shell.

- Compton scattering
- Inner shell excitation
  - Auger electron (light element)
    - Positively affect resolution
  - Fluorescence X-rays (heavy element)
    - Negatively affect resolution
Non-chemically amplified resists

EUV photon

- High-resolution conventional resist such as PMMA utilize this part for the chemical reaction for pattern formation (main chain scission).

- Chemically amplified resists utilize this part for the decomposition of acid generators.

\[
E > E_{th}
\]

\[
E > 25 \text{ meV}
\]

Distribution of radical cation

Resolution blur of L&S pattern

\[
\frac{k_i}{NA} = 0.5
\]
Summary (3)

The wavelength dependence of lithography resolution was investigated in the wavelength region of extreme ultraviolet. The resolution is expected to be highest at a wavelength of 3-5 nm, depending on NA of exposure tools. In the case of low-NA tools, the merit of wavelength reduction from 13.5 nm is significant. However, the merit of wavelength reduction is lost in the case of high-NA tools, particularly when the increase in transparency of the resist with the reduction in wavelength is taken into account. One of the keys to the realization of 6.67nm lithography is the development of high-absorption resists.

Acknowledgement

This work was partially supported by the New Energy and Industrial Technology Development Organization (NEDO).