Feasibility study of sub-10 nm half-pitch fabrication using chemically amplified resist processes of extreme ultraviolet lithography

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Two keywords in the development of resist materials and processes

**Lithography roadmap**

<table>
<thead>
<tr>
<th>Year</th>
<th>2001</th>
<th>04</th>
<th>07</th>
<th>10</th>
<th>13</th>
<th>16</th>
<th>19</th>
<th>22</th>
</tr>
</thead>
<tbody>
<tr>
<td>Line width (nm)</td>
<td>130</td>
<td>90</td>
<td>65</td>
<td>45</td>
<td>32</td>
<td>22</td>
<td>16</td>
<td>11</td>
</tr>
<tr>
<td>LWR (nm)</td>
<td>2.2</td>
<td>1.6</td>
<td>1.1</td>
<td>0.8</td>
<td></td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

**Lithography Solution**

- KrF excimer (248 nm)
- ArF excimer (193 nm)
- ArF excimer Immersion (+DP)
- EUV (13.5 nm)
- EB for mask production

**Radiation chemistry**

- Resolution
- Sensitivity
- LWR(LER)

**Trade-off relationships between resolution, sensitivity, and LER**

**Change of basic science for material design**

- Ionization energy (~10eV)
- Photochemistry
- Radiation chemistry
Concept of chemically amplified resist

Typical components: Partially protected polymer, Acid generator, Quencher

Acid generation through the decomposition of acid generators by exposure

\[ \text{hv, radiation} \]
\[ \text{Ph}_3\text{S}^+\text{X}^- \rightarrow \text{H}^+\text{X}^- \]

Image formation utilizing acid-catalytic chain reaction

Polarity change through deprotection

Termination of chain reaction

High sensitivity is obtained through acid-catalytic chain reaction.
High resolution is obtained through the control of acid diffusion using quenchers.
Role of resist materials
Conversion of energy modulation to binary image

Exposure source
Role of photons:
Transfer of information and energy for imaging
Energy modulation

SEM image of resist

Conversion process

Photon/electron interaction with matter
Energy deposition
Formation of acid image
Decomposition of acid generator

Thermal energy
Formation of latent image
Acid diffusion, deprotection

Solubility change through chemical reaction
Development

Dissolution of molecules

Improvement of resist performance = Improvement of conversion efficiency
Objective

Establishment of scientific foundation and technology for resist characterization of EUV lithography

Ultrashort electron beam
- Time resolution < 1 ps

Modeling

Change of basic science

Time-resolved spectroscopy

Nanopatterning

EUV lithography system
- High-quality optical image
- Spatial resolution < 20 nm

Material information

Trade-off relationships

Server
- 600 cores

Strategy of material design (sub-10 nm half-pitch fabrication)
Analysis of high performance resists (SSR3, 4, 5, 7 and ESR1)

Half-pitch dependence (16 mJ cm$^{-2}$ exposure dose)

Exposure dose dependence (60 nm HP)

Current status of the efficiency of conversion processes
Advanced resist characterization

LER = \frac{0.68\sigma_n}{dm/dx}

Distance, x (nm)

14 mJ cm\textsuperscript{-2}  
15 mJ cm\textsuperscript{-2}  
16 mJ cm\textsuperscript{-2}  
17 mJ cm\textsuperscript{-2}

Stochastic defect generation

Pinching started to appear.

Bridges were eliminated.
Half pitch dependence of stochastic defect generation

Threshold for the elimination of stochastic defect generation in “a SEM image”

Probability for stochastic defect generation rapidly increased with the reduction of half-pitch.

- 22 nm HP
- 16 nm HP
- 11 nm HP
Current status of the efficiency of conversion processes

1. How many photons can be absorbed?
   Absorption coefficient: \( \sim 4 \mu m \)

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: 0.06-0.16 nm
   Activation energy for deprotection
   Activation energy for acid diffusion
   Low-diffusion anion \( \rightarrow \) Anion-bound resist
   High \( T_g \) polymer

4. How smoothly are the polymers dissolved in developer?
   Relationship between LER and chemical gradient, \( f_{LER} \): 0.14-0.31
   Molecular size, protection ratio, dispersion
   Development, rinse

Resist design

\[
LER = \frac{0.68 \sigma_n}{dm/dx}
\]

<table>
<thead>
<tr>
<th>DUV, VUV</th>
<th>EUV</th>
</tr>
</thead>
<tbody>
<tr>
<td>AG</td>
<td>①, ②, ③</td>
</tr>
<tr>
<td>Polymer</td>
<td>③, ④</td>
</tr>
</tbody>
</table>
Fig. Exposure dose dependence of normalized chemical gradient of line-and-space patterns with half-pitch of 7 nm. The optical contrast was 1.0. The effective reaction radius for deprotection was 0.1 nm. The quencher concentration, PEB time, and dissolution point (the normalized protected unit concentration at half the depth of boundaries between lines and spaces) were optimized to maximize the chemical gradient at half the depth of boundaries between lines and spaces.
Dependence of chemical gradient on half-pitch and optical contrast

Fig. Dependence of normalized chemical gradient on half-pitch. The numerical values next to C denote the optical contrast. The optical contrast was changed from 0.6 (bottom line) to 1.0 (top line) in steps of 0.1 for each acid generator concentration. The effective reaction radius for deprotection was 0.1 nm.
Fig. Dependence of LER on half-pitch. The proportionality constant $f_{LER}$ was 0.2. The optical contrast was 1.0. The effective reaction radius for deprotection was 0.1 nm.

- **Increase in AG conc.** = Increase in the number of interaction points of secondary electrons
- Degradation of dissolution kinetics
- Decrease in activation energy for acid diffusion
- Decrease in effective reaction radius for deprotection
Effect of effective reaction radius for deprotection

Fig. Effect of effective reaction radius for deprotection on relationship between LER and half-pitch. The numerical values next to $R_{\text{eff}}$ denote the effective reaction radius for deprotection in nm. The effective reaction radius for deprotection was changed from 0.1 (top line) to 1.0 nm (bottom line) in steps of 0.1 nm. The proportionality constant $f_{\text{LER}}$ was 0.2. The optical contrast was 1.0.

$LER = \frac{0.68\sigma_n}{dm / dx}$

$f_{\text{LER}}$ was assumed to be independent of $R_{\text{eff}}$. 

$1 \times \text{AG}, 30 \text{ mJ cm}^{-2}$

$2 \times \text{AG}, 50 \text{ mJ cm}^{-2}$

$3 \times \text{AG}, 65 \text{ mJ cm}^{-2}$
Fluctuation of number of protected units connected to a polymer molecule

- Number of protected units vs. Distance (nm)
- Standard deviation of the number of protected units connected to a polymer molecule before PEB

- Center of line
- Boundary
- Center of space
This gap should be closed by development factor (Conv. eff. ④).

Current effective reaction radius: 0.06-0.16 nm
Development target of effective reaction radius: 0.4 nm
Fig. Effect of effective reaction radius for deprotection on relationship between optimum PEB time and half-pitch. The effective reaction radius for deprotection was changed from 0.1 (top line) to 1.0nm (bottom line) in steps of 0.1 nm. The optical contrast was 1.0.

Current status of acid diffusion constant

2-10 nm² s⁻¹
The feasibility of chemically amplified resist processes for the sub-10-nm half-pitch node was examined, assuming the use of EUV lithography.

1. With a reduction in half-pitch, LER rapidly increased in the sub-10-nm range. Even if a high-resolution EUV exposure tool is developed, there will be a barrier to sub-10-nm fabrication using chemically amplified resists as long as the current performance of chemically amplified resists is assumed.

2. For the realization of sub-10-nm fabrication, an increase in the number of interaction points of secondary electrons in the resist matrix, namely, an increase in the acid generator concentration, is essential. The development of the technologies required for increasing the acid generator concentration without degrading the other conversion efficiencies is important.

Summary
Acknowledgement

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Details of discussion can be found in

1. T. Kozawa, J. J. Santillan, and T. Itani,
   Feasibility study of sub-10-nm half-pitch fabrication by chemically amplified resist processes of extreme ultraviolet lithography:
   I. Latent image quality predicted by probability density model,
2. T. Kozawa, J. J. Santillan, and T. Itani,
   Feasibility study of sub-10-nm half-pitch fabrication by chemically amplified resist processes of extreme ultraviolet lithography:
   II. Stochastic effects,
   to be submitted to Jpn. J. Appl. Phys.