Optimizing RLS

Seiichi Tagawa

The Institute of Scientific and Industrial Research
Osaka University
and
JST-CREST

IEUVI Resist TWG
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### RLS Trade Off:
The Most Crucial Issue in EUV Resist Development

Many papers have been reported on RLS by a lot of researchers such as R. Brainard, T. Wallow, P. Naulleau, G. Gallatin, et al.

- **Experiments**
  - P. Naulleau et al. SPIE(2006)

- **Simulations**
How to optimize RLS: Fundamental research is essential.

Huge amounts of knowledge infrastructure based on photochemistry are available for photoresists.

New knowledge infrastructure based on radiation chemistry is essential for EUV resists.

Solutions!
One of the best solution is the increase in pattern formation efficiency.

Huge amounts of knowledge infrastructure based on photochemistry are available for photoresists.
Resist pattern formation processes

Exposure

Interaction of radiation (photon, electron etc.) with materials

Conversion of energy to acids

Decomposition of acid generators

Acid diffusion

Deprotection reaction

Latent acid image

Dependent on exposure sources

Acid catalyzed image (Latent image after PEB)

Development

Independent of exposure sources

Proton-anion distribution

Proton

Anion

Position in x-direction (nm)

Position in y-direction (nm)

Exposure sources

Accumulated energy profile

Conversion of energy to acids

Proton-anion distribution

Dependent on exposure sources

Interaction of radiation (photon, electron etc.) with materials
The increase in pattern formation efficiency is required to simultaneously meet the requirements for RLS.

Pattern formation efficiency

Absorption efficiency of incident energy (mainly absorption coefficient of polymer)

Quantum yield of acid

Efficiency of catalytic chain reaction

Other factors: Initial distribution of acid in nanospace and development etc..

Limited by side wall degradation

Limited by secondary electron emission efficiency

Limited by diffusion-controlled rate for chemical reaction
Important point of diffusion length \( (\sqrt{2Dt}) \) and pattern size

It has been believed that a resist with an acid diffusion length of, for example, 15 nm cannot resolve 22 nm patterns. However, this is not true in the presence of quenchers. The resolution does not necessarily depend on the acid diffusion length. Pattern sizes are determined by a initial distribution of acids and quenchers, and ratio between the acid and quencher diffusion constants. (Jpn. J. Appl. Phys. 47 (2008) 4465, 4926, 5404)

The concept of recent quencher controlled CAR is different from classical CAR.

**Acid diffusion and chemical reaction**

\[
\frac{\partial u_{\text{acid}}}{\partial t} = \nabla (D_{\text{acid}} \nabla u_{\text{acid}}) - ku_{\text{acid}} u_{\text{quencher}}
\]

**Base quencher diffusion and reaction**

\[
\frac{\partial u_{\text{quencher}}}{\partial t} = \nabla (D_{\text{quencher}} \nabla u_{\text{quencher}}) - ku_{\text{acid}} u_{\text{quencher}}
\]

**Deprotection reaction, especially rate constant**

\[
[P] = -\int_0^{T_{\text{PEB}}} k_{depro} u_{\text{acid}} [P] dt
\]
Optimization of quencher concentration for each $\alpha$

It has been reported that quenchers affect RLS. However, the details are still unclear.

Fig. Temporal changes of latent images during PEB. The exposure dose is 20 mJ cm$^{-2}$. The quencher concentrations are (a) 81%, (b) 69%, and (c) 53% of initial acid concentration at the origin. The open circles represent the same deprotection profile as the one at $T_{\text{PEB}} = 90$ s in Fig. (b).

Conclusion: the same order of diffusion constants for acids and quenchers are preferable for 22 nm fabrication

Limit of PHS-based chemically amplified resist


Latent images of 22 nm line & space

Intermediate region where protected and deprotected units coexist

The width expands with $1/\sqrt{dose}$ dependence.
Conclusion of the increase in pattern formation by optimizing the catalytic chain reactions

When only the catalytic chain reactions are controlled, 22 nm fabrication is achievable with 10 mJ cm$^{-2}$ exposure dose and a high quality image is unlikely to be obtained with 5 mJ cm$^{-2}$ exposure dose without some special consideration of the catalytic chain reactions and increases in acid generation efficiency and polymer absorption.

The increase in pattern formation efficiency is required to simultaneously meet the requirements for RLS.

Pattern formation efficiency
Absorption efficiency of incident energy (mainly absorption coefficient of polymer)
Quantum yield of acid
Efficiency of catalytic chain reaction

Other factors: Initial distribution of acid in nanospace and development etc.

Limited by side wall degradation
Limited by secondary electron emission efficiency
Limited by diffusion-controlled rate for chemical reaction
Acid Generation of Chemically Amplified EUV Resists

EUV: Main reactions start from ionization of polymer.

Absorption efficiency of incident radiation:
absorption coefficient $\alpha$, ultra thin film (multi-layer resist)

Quantum yield of acid:
concentration of acid generator, dielectric constants, acid amplification, proton formation and transport, counter anion generation efficiency, etc. (Many papers by us)

Nanospace control of acid generation:
Figure 1: Elemental absorption cross-sections at 13.4 nm wavelength. Elements commonly found in photoresist materials are H, C, N, O, F, and S.

Interaction of **EUV photon** with CARs

- spatial distribution -

Intensity of EUV ($I$)

\[ \frac{\partial I}{\partial z} = -\alpha I \]

Absorption coefficient ($\alpha$)

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

EUV photon

\[ \text{photon} \quad \text{Electron} > \text{IP} \quad \text{Electron} < \text{IP} \]

Thermalization Length

4.0 nm for PHS

The number of secondary electrons is estimated experimentally. 4.2 for PHS

Intensity of EUV ($I$)

Inelastic mean free path

<1 nm mean free path at electron with energy > IP

Absorption coefficient ($\alpha$)

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

PHS with 10 wt% TPS-tf Acid molecules per photon: 2.6


Difference between EB and EUV

EB

Isolated pairs (Single spur)

EUV

Multi spur effect

Stronger electric field

Onsager distance
Where the thermal energy of electron correspond to the Coulomb potential.

\[ r_c = \frac{e^2}{\varepsilon kT} \sim 14 \text{ nm} \]

in PHS

(Kozawa et al., J.Appl.Phys, 103(2008)84306)
Electron dynamics in early processes of radiation chemistry

**Ionization**

- Electron with excess energy
- Subexcitational
- Subvibrational

**Parent Radical Cation**

- Geminate Ion Pair
- Low Energy Electron $\sim 0$ eV

**Thermalization**

- Energy exchange, excitation of intermolecular vibration, phonon
- Coulomb Force
- Diffusion

**Modified Smoluchowski equation for CAR**

$$\frac{\partial w}{\partial D t} = \nabla \left( \nabla w + w \frac{1}{k_B T} \nabla V \right) - 4\pi R C w$$

- $w$: Probability density of electrons
- $k_B$: Boltzmann constant
- $V$: Coulomb potential (Dielectric constant)
- $T$: Absolute temperature
- $D$: Sum of diffusion coefficient
- $C$: Concentration of acid generators
- $R$: Effective reaction radius

**Initial distribution function**

$$f(r, r_0) = \frac{1}{r_0} \exp \left( - \frac{r}{r_0} \right)$$

- $r$: Distance between radical cation and electron
- $r_0$: Thermalization distance

Acid generator can react with these low energy electrons.
Fig. Probability density of anion generated in PHS with 10 wt% TPS-tf by (a) an electron and (b) an EUV photon.

**Sensitization distance (ionization)**

<table>
<thead>
<tr>
<th>Distance from EUV absorption point (nm)</th>
<th>Sensitization distance (nm)</th>
<th>Acid generation efficiency (ionization)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EB</td>
<td>5.6 nm</td>
<td>0.74 per ionization</td>
</tr>
<tr>
<td>EUV</td>
<td>6.3 nm</td>
<td>0.62 per ionization</td>
</tr>
</tbody>
</table>

\[
G(\text{acid}) = 3.3 \ (3.3 \text{ acids per 100 eV})
\]

2.6 acids per one photon (92.5 eV) in PHS


Feasibility on High-Sensitivity Chemically Amplified Resist by Polymer Absorption Enhancement


**Current status**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sensitivity</td>
<td>10~20 mJ cm⁻²</td>
</tr>
<tr>
<td>Abs. coefficient</td>
<td>3.8 μm⁻¹ (PHS)</td>
</tr>
<tr>
<td>Thickness</td>
<td>50 nm (40-75 nm)</td>
</tr>
<tr>
<td>Transparency</td>
<td>83%</td>
</tr>
</tbody>
</table>

**Depth profile**

Fig. Depth profile of acid concentration (The number of acid molecules per unit volume). The exposure dose is 10 mJ cm⁻².

**X 1/4**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sensitivity</td>
<td>&lt;5 mJ cm⁻²</td>
</tr>
<tr>
<td>Abs. coefficient</td>
<td>16 μm⁻¹</td>
</tr>
<tr>
<td>Thickness</td>
<td>20 nm</td>
</tr>
<tr>
<td>Transparency</td>
<td>73%</td>
</tr>
</tbody>
</table>

**Side wall degradation**
Reinvestigation is necessary for the relationship between absorption coefficient and side wall angle because of the difference in the sensitization mechanisms of DUV and EUV resists.

We studied the feasibility of high absorption resist process using a simulation from the viewpoint of side wall degradation.

Acid distribution is determined by absorption coefficient.

Moderation through acid diffusion

Restriction in acid diffusion + Effect of secondary electrons

**Electron emission from surface**

Electron emission depends on work function of materials, $W_f$.

EUV photon

Ionization

Total-reflection model : $W_f = \square$

Total-transmission model : $W_f = 0$
**Conclusion:** Compared with PHS-based resists, the fourfold enhancement of polymer absorption is feasible without side wall degradation partly due to the long migration range of secondary electrons, although it is necessary to reduce the resist thickness from 50 to 20 nm.
Conclusion

• To optimize RLS, the improvement of pattern formation efficiency is essential. The efficiency of pattern formation is mainly determined by three factors such as the absorption efficiency of incident radiation, quantum yield of acid, and efficiency of the catalytic chain reactions.

• When only the catalytic chain reactions are controlled, 22 nm fabrication is achievable with 10 mJ cm\(^{-2}\) exposure dose and a high quality image is unlikely to be obtained with 5 mJ cm\(^{-2}\) exposure dose without some special consideration of the catalytic chain reactions and increases in acid generation efficiency and polymer absorption.

• Compared with PHS-based resists, the fourfold enhancement of polymer absorption is feasible without side wall degradation partly due to the long migration range of secondary electrons, although it is necessary to reduce the resist thickness from 50 to 20 nm.

• How to increase the quantum yield of acid is tightly connected with EUV resist reactions and we have published many papers in this field. The most effective method in this part is increasing in acid generator concentration, but we didn’t talk about it because of time limitation.

• Resist makers started the improvement of EUV resists based on above concept. The good improvement on RLS has been achieved recently.

• The fundamental concept of optimizing RLS is made clear, however, there are many remaining problems to optimize RLS.