Trade-off Problems among Resolution, LWR and Sensitivity of EUV Resists

Tagawa\textsuperscript{1,2}

\textsuperscript{1} The Institute of Scientific and Industrial Research, Osaka University, 
\textsuperscript{2} Japan Science and Technology Agency, CREST, c/o Osaka University,  
8-1 Mihogaoka, Ibaraki, Osaka 567-0047, Japan  
tagawa@sanken.osaka-u.ac.jp

Approaches to address the EUV resist challenges of image collapse, LWR, sensitivity, and resolution  
October 17-20, 2010  
Kobe, Japan
Acknowledgement


Osaka University

• (New Laboratory) Beam Application Frontier Laboratory (Director) Drs. H.Yamamoto, K. Enomoto, Prof. Endo et al.
• Nanofabrication Function (Head), Handai Multi-Functional Nanofoundry Nonotechnology Dr. A. Oshima et al.
• Research Laboratory for Quantum Beam Science: Pulse Radiolysis Facility Selete (Semiconductor Leading Edge Technologies)

Researchers in Industrial Companies and Universities

Waseda University (Guest Professor) Prof. M. Washio, Graduate Students (T. Gowa.)

EUV resist net of URVIC (University, Research Institute, Venture Company, Industry, Consortia) net (Chairman)

Old coworkers: Prof. Tabata, past students (Profs. M. Washio & Y. Yoshida), NTT resist researchers
## Critical Issues and Requirements of EUV Resist Development

<table>
<thead>
<tr>
<th>Past and Now:</th>
</tr>
</thead>
<tbody>
<tr>
<td>RLS (Resolution, LWR and Sensitivity) trade-off problem.</td>
</tr>
<tr>
<td>Increase in pattern formation efficiency</td>
</tr>
<tr>
<td>Image collapse</td>
</tr>
<tr>
<td>Outgas</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Near Future:</th>
</tr>
</thead>
<tbody>
<tr>
<td>The reduction of LWR</td>
</tr>
<tr>
<td>Increase in chemical gradient and decrease in chemical inhomogeneity at image boundary</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Future:</th>
</tr>
</thead>
<tbody>
<tr>
<td>The more detailed research on nanospace reactions and molecular interactions in EUV and EB resists</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Always:</th>
</tr>
</thead>
<tbody>
<tr>
<td>Industries want the help of radiation chemists for not only solutions of high sensitive resists but also many problems such as radiation damages and radiation-induced contamination.</td>
</tr>
</tbody>
</table>
What is RLS Trade-off Problem
The Most Critical Problem of EUV Resist Development Today

5mJ/cm² EUV resists were required for early stage of EUV lithography development. Chemically amplified resists were considered to be candidates, but the resolution limit of chemically amplified resists were considered to be 50/60 nm at that time.

After the development of the EUV chemically amplified resists with sub-50 nm resolution started, many researchers had arrived at the RLS (Resolution, LWR, Sensitivity) trade-off triangle around 2003.

Many experimental results were reported: For example, Brainard et al., Proc. SPIE (2004), Pawloski et al., Proc. SPIE (2004)

It was very difficult to improve resolution, LWR, and sensitivity, simultaneously. Resist development almost stopped several years at that time.
What is the Origin of RLS Trade-off Problem

- It occurred in chemically amplified resists (CARs) with high concentration of quenchers for sub-50 nm resolution.
- From the early stage of the industrial use of chemically amplified resists, amines have been contained in CARs for measures against so-called post-exposure delay effects due to surface contamination from airborne amines.
- Very high concentrations of amines are required for getting high resolution CARs less than 50 nm resolution.
- High concentration of amines improves resolution and LER, but sensitivity decreases and trade-off among resolution, LER and sensitivity (so-called RLS trade-off) was induced.
- At that time, only EUV resists required less than 40 nm resolution. So RLS trade-off appeared in EUV resist research at first.
The Origin of RLS

• RLS trade-off appeared in EUV resist research at first.

• In the beginning, there was confusion. Is RLS trade-off specific in EUV resists or not?

Reaction mechanisms change from photochemistry to radiation chemistry.
Simulation (mathematics) by Gallatin in 2005 clearly explained RLS trade-off without acid generation mechanisms. In simulation, no fundamental differences exist among ArF, EB and EUV resists after acid generation.

RLS trade-off is not specific.

Therefore, most of resist researchers except for us studied processes mainly after acid generation in early research stage of RLS Trade-off problem.

But we thought the acid generation mechanisms, especially nano-space (geminate recombination) reactions are important and essential for the solution of RLS trade-off problem, because the high acid yield and the small acid space distribution are clearly the best solutions of RLS trade-off problem.
Resist pattern formation processes

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

Exposure (Tool)

Acid generation

Accumulated energy profile

Acid formation processes.
Processes depend on exposure tool

Latent acid image

Acid catalyzed image (Latent image after PEB)

Acid diffusion, Deprotection reaction

Development

Other Treatments:
Rinse, Vapor smoothing, Hardbake, Ectch, Ozonation, etc.

The high acid yield and the small acid space distribution are determined in acid formation processes.
Snapshots of the performed Monte Carlo and dissolution simulations. (a) Initial spatial distribution of protons (green) and counter anion (red) produced by EB exposure. (b) Latent images after PEB (c) Positive-type line pattern after development.

RLS relationship of developed line pattern at optimized PEB and development time. The exposed line widths of (a) and (b) are 30 and 10 nm, respectively.

The trade-off RLS relationship is successfully reproduced under the optimized condition of PEB and development time by Monte Carlo and dissolution simulation including radiation chemical reactions under simple boundart conditions. [A. Saeki, T. Kozawa, and S. Tagawa, *Appl. Phys. Express* 2 (2009) 075006.]
Resist pattern formation processes

Interaction of radiation (photon, electron etc.) with materials
Acid generation
Acid diffusion, Deprotection reaction

Exposure (Tool)
Accumulated energy profile
Latent acid image
Acid catalyzed image (Latent image after PEB)
Development
Other Treatments: Rinse, Vapor smoothing, Hardbake, Ectch, Ozonation, etc.

The high acid yield and the small acid space distribution are determined in acid formation processes.
The increase in pattern formation efficiency is required to simultaneously meet the requirements for solution of RLS trade-off problem.

Pattern formation efficiency before acid generation

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

Quantum yield of acid

Exposure source dependent

Limited by side wall degradation

Limited by secondary electron emission efficiency
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\(^{-1}\)

-EUV photon (92.5 eV)-

\(\text{Electron} > \text{IP}\)

\(\text{Electron} < \text{IP}\)

-Ionization-

-Thermalization-

-Excitation-

-Multi spur effect-

Inelastic mean free path

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

Thermalization Length

4.0 nm for PHS

The number of secondary electrons is estimated experimentally.

4.2 for PHS

PHS with 10 wt% TPS-tf

Acid molecules per photon:

2.6 (Kozawa et al. J.Vac.Sci. Tecnol.,B25(2007) 2481)

**Results**

<table>
<thead>
<tr>
<th>Wt% of Fluorine atom per Fluorinated polymer</th>
<th>Absorption coefficient (μm⁻¹)</th>
<th>Acid yield</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Caluculation value</td>
<td>Experimental value</td>
</tr>
<tr>
<td>63</td>
<td>9.9</td>
<td>7</td>
</tr>
<tr>
<td>51</td>
<td>8.9</td>
<td>8.6</td>
</tr>
<tr>
<td>38</td>
<td>7.8</td>
<td>8.1</td>
</tr>
<tr>
<td>25</td>
<td>6.6</td>
<td>6.6</td>
</tr>
<tr>
<td>0</td>
<td>3.8</td>
<td>4</td>
</tr>
</tbody>
</table>

**Fig. Depth profile of acid concentration (the number of molecules per unit volume) calculated on the basis of experimental data of acid generation efficiency and absorption coefficients at the exposure dose of 5 mJ/cm².**

Theoretically the yield is 2.6 times based on photoabsorption process, but experimentally 1.5 times. The control of the reaction mechanism is not enough until at that time

**Ultra thin film resists is important.**

[H. Yamamoto et al. APEX 1 (2008) 047001.]
Clarification of Electron Flow in Chemically Amplified Resist

EUV

PF⁺

Fluorinated polymer

Ionization

Recombination

$e^-$

Decomposition of acid generator (RX)

RX

$X^-$

$R_{AG}$

Electron attachment

Radical anion formation

$p_1$

Electron transfer

$p_2$

Dissociation

PF

F⁻

RX

Acid generation

$R$: Effective reaction radius

$p$: Probability ($p_1 + p_2$ = 1)

depends on the lifetime of PF radical anion
Radiation Chemistry of Fluorinated Aromatic Compounds

Fig. Transient absorption spectra of 100 mM 8FN solution in THF. (♦; immediately after the pulse (0 ns) ■; 50 ns ▲; 150 ns ×; 300 ns).

Fig. Transient absorption spectra of 100 mM 1FN solution in THF. (♦; immediately after the pulse (0 ns) ■; 50 ns ▲; 150 ns ×; 300 ns).
EUV Mechanism\(^1\) Provides RLS Gain?
(from Todd R. Younkin, Intel, Litho Forum 2008)

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

\(^1\)Kozawa, et al. JVSTB 25, 2481 (2007)
Investigation on nanoscale topography in resist

**Interaction of electron with material -spatial distribution-**

- **Excitation**
- **Ionization**
- **Onsager distance**
- Mean value of the initial separation length between the electron and the radical cation is \( 4 \text{ nm} \) in PHS

Where the thermal energy of electron correspond to the Coulomb potential,

\[
r_c = \frac{e^2}{\kappa T}
\]

\( \sim 14 \text{ nm} \) in PHS

Small part of electrons become free.

\[
\text{RH} \rightarrow \text{RH}^+ + e^- \\
\text{RH}^+ + e^- \rightarrow \text{RH}^*
\]

**Electron**

We elucidated the formation mechanism of resist pattern from the viewpoints of the interaction of EB reaction with films based on huge amount of experimental results such as pulse radiolysis, subsequent radiation chemical reactions, and diffusive reactions

Establishment of basic science for material development and process/device design
Snapshots of the performed Monte Carlo and dissolution simulations. (a) Initial spatial distribution of protons (green) and counter anion (red) produced by EB exposure. (b) Latent images after PEB (c) Positive-type line pattern after development.

RLS relationship of developed line pattern at optimized PEB and development time. The exposed line widths of (a) and (b) are 30 and 10 nm, respectively.

The trade-off RLS relationship is successfully reproduced under the optimized condition of PEB and development time by Monte Carlo and dissolution simulation including radiation chemical reactions under simple boundary conditions. [A. Saeki, T. Kozawa, and S. Tagawa, Appl. Phys. Express 2 (2009) 075006.]
Many kinds of methods to improve RLS trade-off and LWR.

• High Absorption
• High Yields of Acids
• Diffusion Control Reactions
• Improvement of Development
• Polymer-bound PAG Resist System
• Variable Acid Diffusion Type Resists
• Treatments after Development
• Molecular Resists
• Many Other Methods
Today critical issues and requirements of EUV resist development past and now, that is, how to solve RLS trade-off and how to increase in pattern formation efficiency are summarized.

Nanospace radiation chemistry of EUV resists is important and essential in understanding the resist pattern formation mechanisms.


The improvement at each stage is required cloth to its physical and chemical limit.
Anisotropic acid diffusion

Diffusion coefficient depends on matrix.

In high dose region, the environment surrounding acid molecules significantly changes during the catalytic chain reactions.

- Nonpolar to polar
- Generation of byproducts (low molecular contents)
- Increase in free volume etc.

Anisotropic diffusion

Diffusion coefficient depends on matrix.

- Nonpolar to polar
- Generation of byproducts (low molecular contents)
- Increase in free volume etc.

What is STAR polymer?

A) The core unit contains an acid cleavable group. The arm unit is a partially protected linear polymer.

B) The core unit is decomposed first.

C) The acid labile group of the arm unit is also decomposed.

Chemical concept for STAR shaped polymer
Lithographic performance comparison (Resolution)

Resolution comparison of Linear and STAR polymer

<table>
<thead>
<tr>
<th></th>
<th>30nmHP</th>
<th>28nmHP</th>
<th>26nmHP</th>
<th>24nmHP</th>
<th>22nmHP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Linear25-M</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Esize ~ 18.4mJ</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LWR=4.4nm</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>UR ~ 30nm HP</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DOF ~ 120nm</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>STAR25-M</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Esize ~ 16.8mJ</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LWR=4.1nm</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>UR ~ 28nm HP</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DOF ~ 230nm</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Lithographic Condition
- Exp. Tool: Micro Exposure Tool
- Substrate: B-ARC
- Resist thickness: 60nm
- PAB: 80°C-60s
- Illumination: NA 0.3, Annular
- PEB: 80°C-60s
- Development: TMAH 2.38%aq, 60s


SPIE Advanced Lithography Feb. 24, 2009
Sensitivity and Shot Noise of CAR and non-CAR.

5 mJ/nm² is about 3 EUV photons/(1 nm)².

It is very difficult to overcome shot noise problem in non-CAR.

In CAR, the recombination reaction of acids and quenchers occurs in image boundary. LER is determined at image boundary. Acid diffusion decreases shot noise in CAR.

Initial acid distribution (high $E_a$ resist)

Fig. The aerial image of incident EUV (arb. unit) and the initial acid distribution (molecule nm⁻³).