Fundamental aspects of CAR, PSCAR and new PSCAR for overcoming problems of RLS trade-off and stochastic defects

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• High sensitivity for high throughput is very important.

• Stochastic defects is one of the most critical items of EUV lithography near future.

• There is no clear solutions for stochastic defects problem.

• The new PSCAR process shows the possibility not only getting high sensitivity with keeping constant or higher resolution and also the possibility of overcoming or reducing the stochastics problems.

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In simulations of CAR, G.M. Gallatin, Proc. SPIE (2005), showed no fundamental differences in simulations among ArF, EB and EUV resists after latent acid image formation\(^5\). Therefore, the latent acid image is very important.
**Reaction mechanisms of EUV and photo resists**

- **EUV resists (Main process)**

  **Ionization channel**
  
  \[ \text{RH} \rightarrow \text{RH}^+ + e^- \rightarrow \text{R}^+ + \text{RHH}^+ + e^- \]
  
  \[ \text{Ph}_3\text{S}^+X^- + e^- \rightarrow \text{Ph}_2\text{S} + \text{Ph}^- + X^- \rightarrow \text{Ph}_2\text{S} + \text{Ph}^- + \text{H}^+X^- \]

- **Photoresists (Main process)**

  **Excitation channel**
  
  RH: Solvent
  
  Homolysis
  
  \[ \text{Ph}_2\text{S}^+ + \text{Ph}^- + X^- \rightarrow \text{Ph}_2\text{S} + \text{Ph}^- + \text{H}^+X^- \]

  Heterolysis
  
  \[ \text{Ph}_3\text{S}^+X^- \rightarrow \text{Ph}_2\text{S} + \text{Ph}^- + X^- \rightarrow \text{Ph}_2\text{S} + \text{Ph}^- + \text{H}^+X^- \]

  \[ \text{Ph}_2\text{S} + \text{Ph}^+ + X^- \rightarrow \text{Ph}_2\text{S} + \text{Ph}^+ + \text{H}^+X^- \]

  \[ \text{Ph}_3\text{S}^+X^- \rightarrow \text{Ph}_2\text{S} + \text{Ph}^+ + X^- \rightarrow \text{Ph}_2\text{S} + \text{Ph}^+ + \text{H}^+X^- \]

  \[ \text{X} \rightarrow \text{Ph}_2\text{S} + \text{Ph}^+ + X^- \rightarrow \text{Ph}_2\text{S} + \text{Ph}^+ + \text{H}^+X^- \]

1. Dissociative electron attachment reaction
2. Geminate ion recombination

S. Tagawa, et.al. SPIE 3999 (2000) 204

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Resist Sensitivity Improved 30-50% via Addition of EUV Sensitizing Agents.

No Loss In Resolution or Degradation in LWR

Multiple Suppliers Achieving Similar Results in 1H’08


Resist A
S=27.5 mJ; L<5.5 nm

Resist B
S=14.0 mJ; L<5.0 nm

EUV Mechanism\(^1\) Provides RLS Gain?

\(^1\)Kozawa, et al. JVSTB 25, 2481 (2007)
Based on the resist pattern formation model of EUV CARs including radiation chemistry, the RLS trade-off has been improved steadily by worldwide efforts. This approach is reaching near physical limit of the model around 2013. Therefore, novel processes and materials of overcoming RLS trade-off must be necessary for EUVL HVM.

A new high resist sensitization process by the combination lithography of EUV pattern exposure with UV flood exposure of *Photosensitized Chemically Amplified Resist (PSCAR)* was proposed at Osaka University in 2013. (S. Tagawa et al., J. Photopolym. Sci. Tech. 26, 825 (2013)

**CAR reactions:** EUV exposure (radiation chemistry)④

**PSCAR reactions:** EUV Pattern exposure④ + UV flood exposure(photochemistry)④

The latent acid image is still very important.

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1. The first EUV pattern exposure produces photosensitizers (PSs).
2. Non irradiated resist has no absorption band at the second flood exposure light wavelength. Therefore, no reaction of resist occurs by only the second flood exposure.
3. Only PSs have absorption bands at the second flood exposure wavelength. Sensitivity enhancement occurs by excitation of PSs.

One example of PP and PS for PSCAR and their reaction and UV-Vis spectra (Tomoki Nagai, et. al., Proc. SPIE, 9779-7 (2016))
Breakthrough of RLS trade-off

Schematic drawing of (1) RLS trade-off and (2) initial distributions and yields of acid.

If initial acid yield increases from (A) to (B) with the same distribution, RLS trade-off is improved from (A) to (B). (S. Tagawa, SPIE Newsroom, 13 March 2014)

**Simulations:** G.M. Gallatin, *Proc. SPIE* (2005), (no fundamental differences in simulations among ArF, EB and EUV resists after latent acid image formation.)

The higher acid yield with the same acid space distribution is clearly one of the best solutions of RLS trade-off problem further.

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The process for high yield and small size latent acid image is important for EUVL HVM.

Therefore, a new high resist sensitization process by the combination lithography of EUV pattern exposure with UV flood exposure of *Photosensitized Chemically Amplified Resist*™ (PSCAR™) was proposed at Osaka University in 2013 (S. Tagawa et al., J. Photopolym. Sci. Tech. 26, 825 (2013)).

In SPIE Advanced Lithography, PSCAR optimization to reduce EUV resist roughness with sensitization
Paper 10960-9
Time: 10:30 AM - 10:50 AM
Author(s): Seiji Nagahara et al.
Imec researchers reported on random defects with EUV at 5 nm. Click to enlarge. Source: Imec.

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New Process

Combination of EUV pattern exposure and UV flood exposure

1. The resist of the new process containing precursor of photosensitizer (PPS), PAG and PBG (photo base generator).
2. EUV pattern exposure produces photosensitizer (PS).
3. Only PS and PBG have absorption bands at UV flood exposure wavelength. Both acids and bases are generated by second flood exposure excitation of PS and PBG.

The new process was now carried out by stand-alone flood exposure system and home-made materials in University. The new process will be developed by the in-line flood exposure system and resist materials made by industries.

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The new process getting higher sensitivity with keeping the same resolution by UV flood exposure (One example)

\[ \text{Acid distribution produced by UV flood exposure & EUV exposure (A + a)} \]

\[ \text{Photosensitizer distribution} \]

\[ b/a = (B + b)/(A + a) \]

\[ (A + a) - (B + b) < (A + a) - (B + b) \]

Even if \((\text{Quencher concentration} / \text{Acid concentration})\) is constant, latent acid concentration at center part \(\text{(Acid concentration} - \text{Quencher concentration})\) always increase with flood exposure.

A: acids produced by UV flood exposure, a: acids produced by EUV pattern exposure, B or B’: quenchers produced from PBG by UV flood exposure, b: initial quencher

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Conclusion

• The new PSCAR processes can produce much higher concentration of photosensitizer (PS) than other PSCAR because of low quencher concentration during EUV exposure. It is good for stochastic problems.

• Higher PS can reduce flood exposure dose. The lower flood exposure dose is good for UV flood exposure side reaction problems. It is good for random noise problems.

• The new PSCAR processes can keep constant pattern resolution even for higher dose based on the control of the ratio of acid yields to quencher yields. EUV pattern exposure determine the pattern size and the new PSCAR flood exposure process getting high sensitivity without losing resolution. The new PSCAR has the possibility of overcoming or reducing the stochastics problems such as missing and kissing contact holes and micro-bridge and line braking of line/space.
Acknowledgments

We would like to acknowledge members of collaboration members of PSCAR process, especially members of Osaka University, Tokyo Electron Ltd., Tokyo Electron Kyushu Ltd., Tokyo Electron America, Inc., JSR Corporation, JSR MICRO NV, imec, and Paul Scherrer Institute, ASML.

New PSCAR concept promising high sensitivity resist overcoming problems of RLS trade-off, LER and stochastic defects

Paper 10960-13
Time: 11:50 AM - 12:10 PM
Author(s): Seiichi Tagawa, Osaka Univ. (Japan)
Thank you for your kind attention.
Blur distance: Distance between ionizations, Diffusion length of acid reacting with polymers and base during PEB > ①Thermalization length of e⁻ > new processes (② thermal reaction distance (at RT), Electron transfer distance from PS* to PAG)

Ununiformity of acid around pattern edge: In CAR and PSCAR, stochastic problem is important only around pattern edge. The acid number reacting with polymers and base around pattern edge during PEB is much larger than initial number of acid around pattern edge just before PEB.
Stochastics (Random Noise) Problems

Roughness (LER, CER) due to photon shot noise can be explained by using
\[ \text{Roughness(LER,CER)} \propto \sigma_{\text{photon shot noise}} \frac{1}{\text{dm/dx}} \]

1. New process has very sharp chemical gradient \((\text{dm/dx})\) reducing roughness.

Diffusion coefficient depends on matrix. □ Anisotropic diffusion □ High chemical gradient

2. New process has the large numbers of intermediates (acids and quenchers) at image boundary reduce random noise at image boundary (\(\sigma_{\text{photon shot noise}}\)).

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The new process getting higher sensitivity with keeping the same or higher resolution by UV flood exposure

Total yields of acids, quenchers and photosensitizer of PSCAR containing PBG. Acids produced by UV flood exposure (A) and EUV pattern exposure (a). Quencher yields are the sum of quenchers produced from PBG by UV flood exposure (B or B’) and initial quencher (b)

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EUV pattern exposure producing acids and photosensitizer. Neutralization of acid and quencher producing latent acid and quencher distribution.

Distribution of acid generated by EUV exposure and quencher distribution in PSCAR containing PBG

Distribution of acids and quenchers of PSCAR (high Ea) containing PBG after neutralization of acids and quenchers at room temperature and before UV flood exposure

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