Fundamental aspects of RLS trade-off and photon shot noise of CAR and PSCAR

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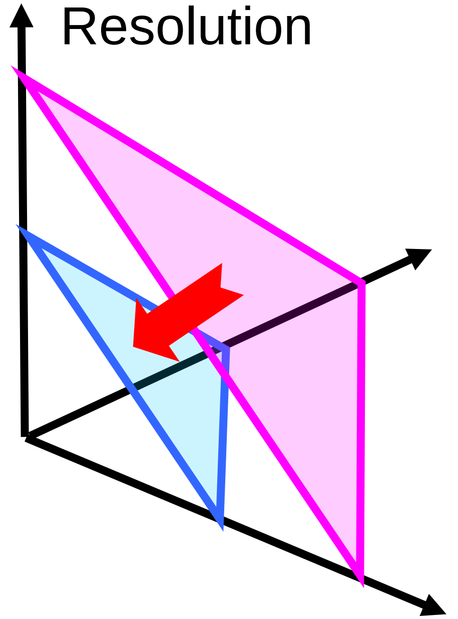
Critical Problems of Next Generation EUV Lithography

1. **The most important critical issue of EUV lithography is the weak intensity of EUV source.**
2. **The resist sensitivity and the exposure light intensity are complimentary. Therefore high sensitization of EUV resists is required.**
3. **However, dramatic enhancement of resist sensitivity is widely confirmed to be difficult due to both RLS trade-off and photon shot noise problems.**



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

❷ **Photon Shot Noise Problem**: LER and photon hsot noise in intermediate region can be approximated by using chemical gradient for high sensitive CAR.

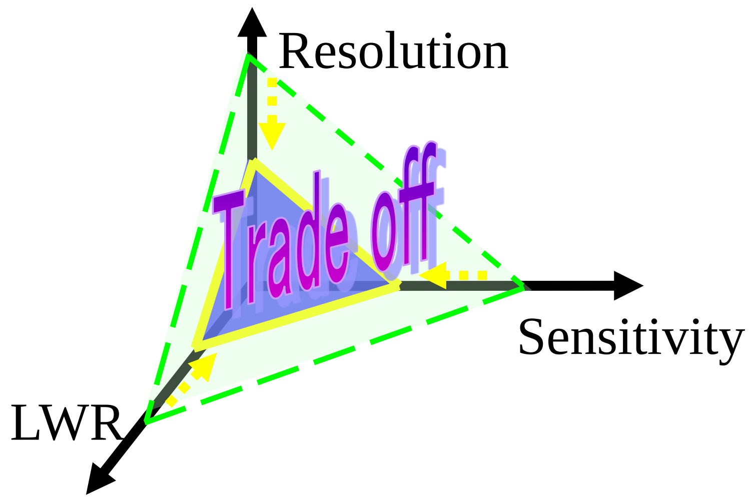
$LER_{photon\ shot\ noise} \propto \sigma_{photon\ shot\ noise}/dm/dx$

Resist TWG at EUVL Symposium 2016

There are two important points in EUV resists

(1) ❶RLS trade off problem

The most difficult technical requirement
for EUV resist is simultaneous improvement in resolution, LWR, and sensitivity (RLS).



(2) Change of resist reaction mechanisms

The photon energy of EUV (13.5 nm, 92.5 eV) is much higher than ionization potential of resist materials (~10 eV).
Reaction mechanisms change from photochemistry to radiation chemistry. (A review paper : Kozawa and Tagawa, 2010)

Big Difference Between Reaction Mechanisms of EUV (EB) Resists and Photoresists

· EUV and EB resists（Main process）

Ionization channel

$RH \rightsquigarrow RH^{+\cdot} + e^- \xrightarrow{RH} R^{\cdot} + RHH^+ + e^-$

$Ph_3S^+X \xrightarrow{e^-} Ph_2S + Ph^{\cdot} + X^- \xrightarrow{H^+} Ph_2S + Ph^{\cdot} + H^+X^-$

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

·Photoresists（Main process）

Exicitation channel

RH: Solvent

$Ph_2S^{\cdot +} + Ph^{\cdot} + X^- \xrightarrow[\text{cage-escaped}]{} Ph_2S + Ph^{\cdot} + H^+X^-$

Homolysis

$(Ph_3S^+X^-)^* \rightarrow Ph_2S^{\cdot +} + Ph^{\cdot} + X^-$ (in-cage Reconbination) $\rightarrow$ *o* -PhPhSPh + H^+X^-, *m* -PhPhSPh + H^+X^-, *p* -PhPhSPh + H^+X^-

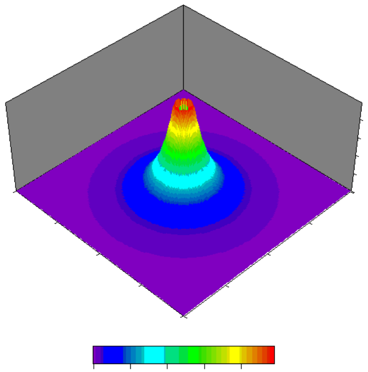
Heterolysis

$(Ph_3S^+X^-)^* \rightarrow Ph_2S + Ph^+ + X^-$ (in-cage)

in-cage

$Ph_2S + Ph^+ + X^- \xrightarrow[\text{cage-escaped}]{RH} Ph_2S + PhR + H^+X^-$

Acid generation is very fast and mainly produced in nanospace.

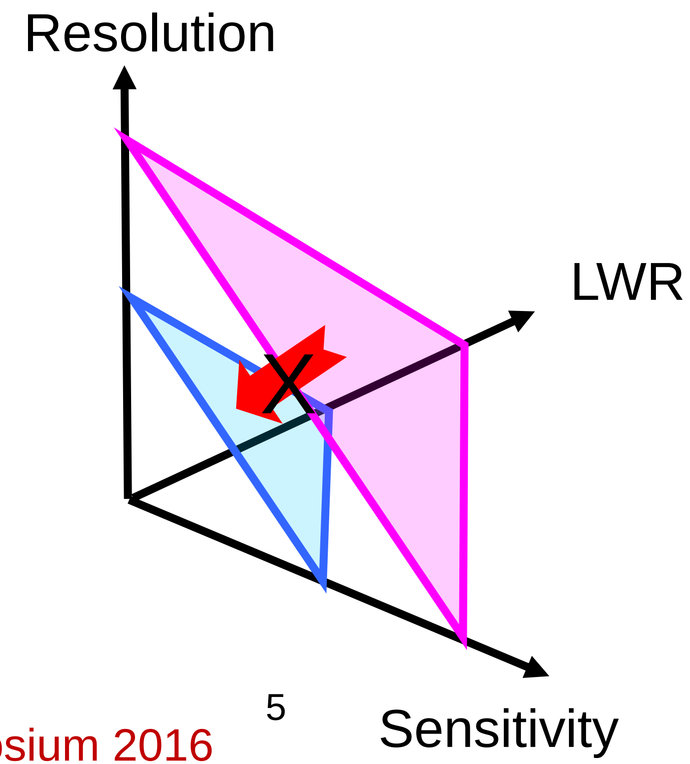


❶RLS (Resolution, Line Width Roughness , Sensitivity) Trade-off Problem

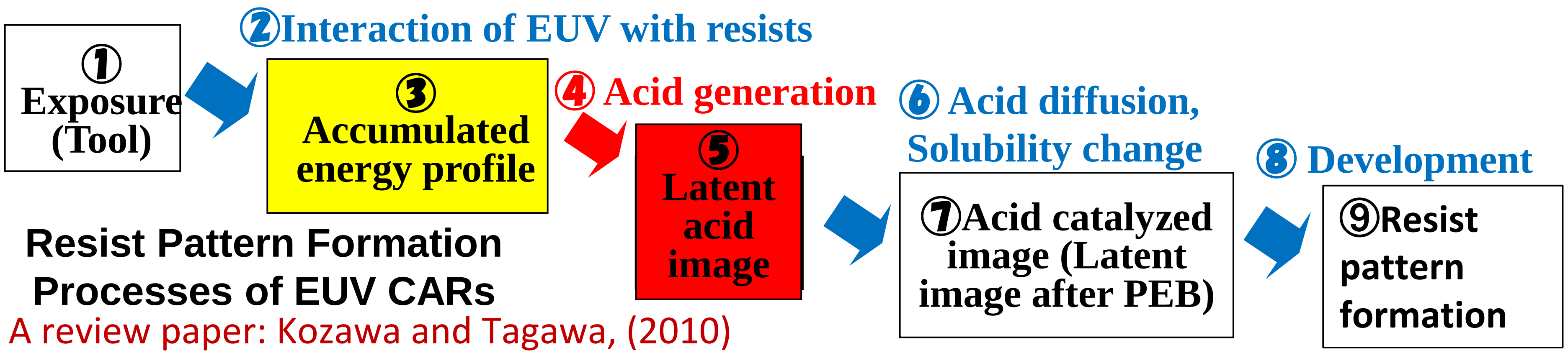
1. Around 2000, the limitation of resolution was determined by acid diffusion length around 40-50 nm. EUV resists required less than 40 nm resolution. Easy method for getting high resolution is controlling acid diffusion length by high concentration quenchers.

2. So-called RLS trade-off appeared in EUV resist research at first. Many researchers on EUV chemically amplified resists (CARs) had arrived at the RLS trade-off triangle around 2003. **Many experimental results**: For example, *Brainard et al., Proc. SPIE (2004), Pawloski et al., Proc. SPIE (2004), Wallow et al., Proc. SPIE (2008)*

3. Simulation by Gallatin clearly explained RLS trade-off. (G.M. Gallatin, Proc. SPIE 5754 (2005) 38.)



One of Solutions of ❶RLS Trade-off Problem:CAR



Resist Pattern Formation Processes of EUV CARs

A review paper: Kozawa and Tagawa, (2010)

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 now reaching near physical limit of the model. Therefore, novel processes and materials of overcoming RLS trade-off must be necessary for EUVL HVM.

One of Solutions of ❶RLS Trade-off Problem is PSCAR

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

The high acid yield and the small acid space distribution are clearly the best solutions of RLS trade-off problem.

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

CAR: Pattern exposure + thermal reaction ➡ PSCAR: (Pattern + flood exposure) + thermal reaction

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One of Solutions of ❶RLS Trade-off Problem is a new process

A high resist sensitization process by the combination lithography of EUV or EB pattern exposure with UV flood exposure of *Photosensitized Chemically Amplified Resist*™ (PSCAR™) was proposed at Osaka University in 2013.

(S.Tagawa et al., J.Photoplm. Sci. Tech. 26, 825 (2013))

1. The first EUV pattern exposure produces photosensitizers (PSs).

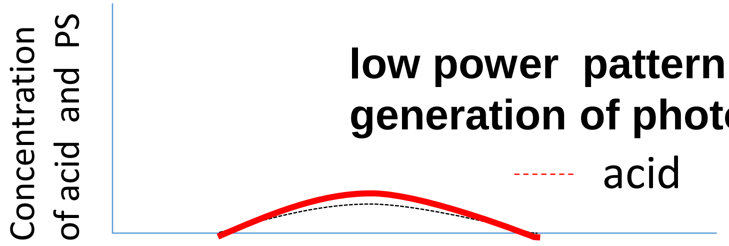
2. Resist has no absorption band at the second flood exposure light wavelength. Therefore, no reaction of resist occurs by only the second flood exposure.

3. Only PSs have absorption bands at the second flood exposure wavelength. Sensitivity enhancement occurs by excitation of PSs.

New Process: Combination of radiation chemistry with photochemistry

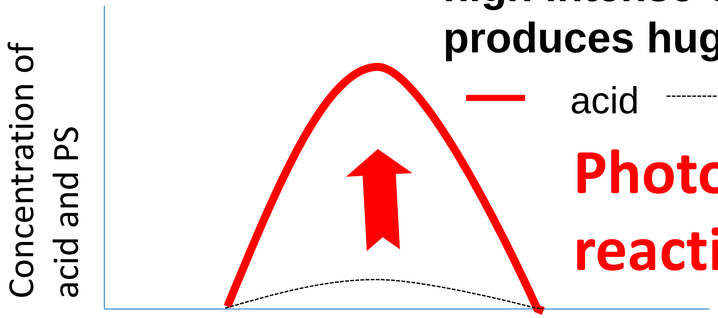
(1st exposure)

low power pattern exposure→ generation of photosensitizer (PS) and acid



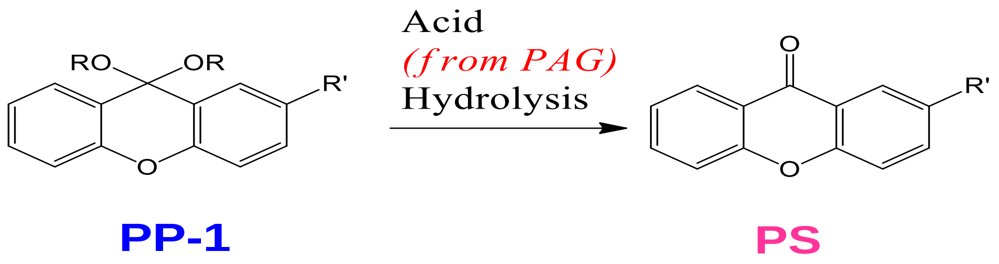
(2nd exposure)

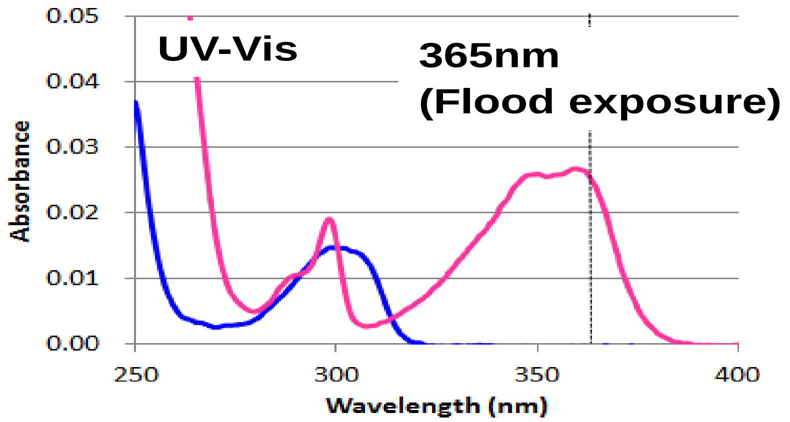
high intense UV flood exposure produces huge amount of acid



Photosensitized acid generation reactions at room temperature

One example of precursor(PP) of PS and PS

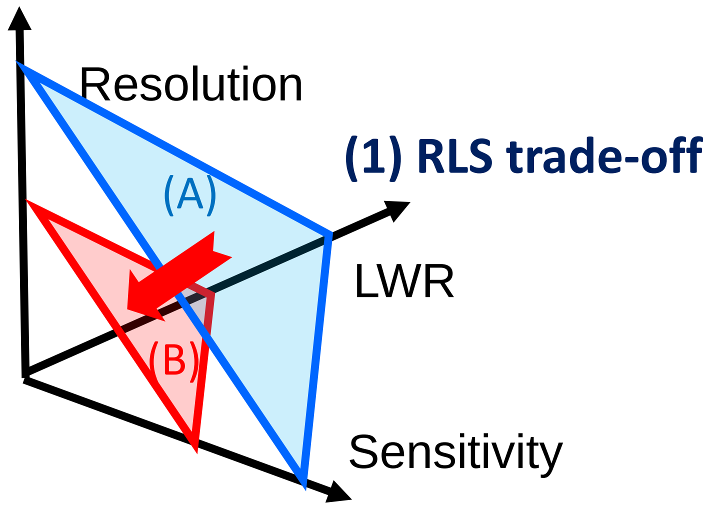


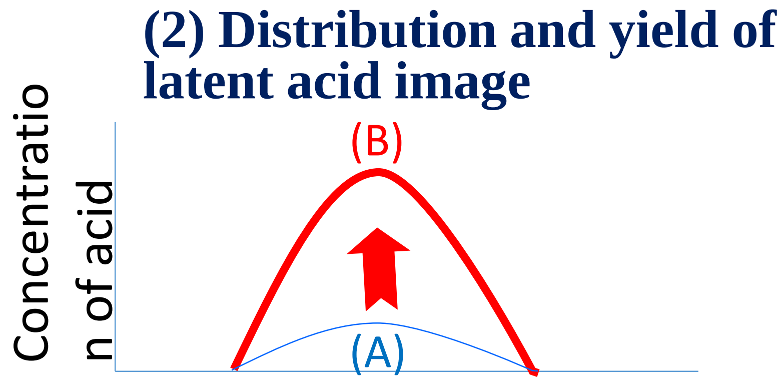


One example of PP and PS and their reaction and UV-Vis spectra

1. The first EUV pattern exposure produces photosensitizers (PSs).
2. 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.

Breakthrough of RLS trade-off





Schematic drawing of (1) RLS trade-off (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 high acid yield and the small acid space distribution are clearly the best solutions of RLS trade-off problem.

For example, the higher concentration of quencher can be used at same resist sensitivity. Then, the higher chemical gradient can be obtained. The higher contrast and suppressing photon shot noise can be obtained.

❷ Photon Shot Noise Problem

PSCAR™

The higher acid concentration and chemical gradient can be obtained by PSCAR process.

There are so many papers on photon shot noise.

Normalized image log slop (NILS) = w x d(lnI)/dx
w: nominal line width, I: intensity of insident photons
For example: C.A.Mack, Field Guide to optical lithography (2006), many papers
Modified NILS (NILS*) is better for EUVL/EB lithography, Kozawa and Tagawa (2009)

LER and Photon Shot Noise

LER can be approximated by using chemical gradient (dm/dx) experimentally
$LER = f_{LER}$ (constant) /dm/dx   Kozawa, Oizumi, Itani, Tagawa (2010)
The LER originating from the fluctuation of chemical reactions (LER_{CG}) increases with increasing resist sensitivity experimentally   Kozawa, Yamamoto, Tagawa (2010)

Therefore, LER and photon shot noise in intermediate region can be approximated by using chemical gradient for high sensitive CAR.

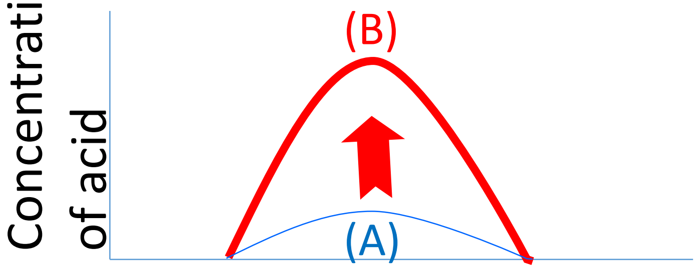
$LER_{\text{photon shot noise}} \propto \sigma_{\text{photon shot noise}}/dm/dx$

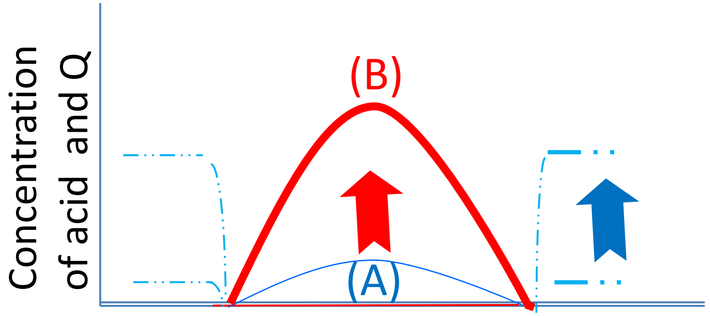
Breakthrough of ❷Photon Shot Noise Problem

LER and photon shot noise in intermediate region can be approximated by using chemical gradient for CAR.

$$LER_{\text{photon shot noise}} \propto \sigma_{\text{photon shot noise}}/dm/dx$$

Distribution and yield of latent acid image





Schematic drawing of acid generation processes of PSCAR resist by the combination of 1st EB or EUV pattern exposure with 2nd photon flood exposure. The limitation of acid diffusion by high concentration quencher (Q) is necessary for high resolution pattern formation in PSCAR. Therefore, the higher chemical gradient (dm/dx) can be obtained.

CAR: Pattern exposure + thermal reaction ➡ PSCAR: (Pattern + flood exposure) + thermal reaction

$\sigma_{\text{photon shot noise}}$ at **Pattern exposure** of CAR is the same as $\sigma_{\text{photon shot noise}}$ at **(Pattern + flood exposure)** of PSCAR, but the number of acids is different.

Therefore, $\sigma_{\text{photon shot noise}}$ after random walk thermal diffusion reactions of PSCAR is smaller than $\sigma_{\text{photon shot noise}}$ of CAR.

Conclusion

- PSCAR is good solution for both RLS trade-off and photon shot noise problems.
- Optimization of materials and processes takes much time.