# Fundamental aspects of *Photosensitized chemically amplified resist* (PSCAR) and CAR: How to overcome RLS trade-off and photon shot noise problems

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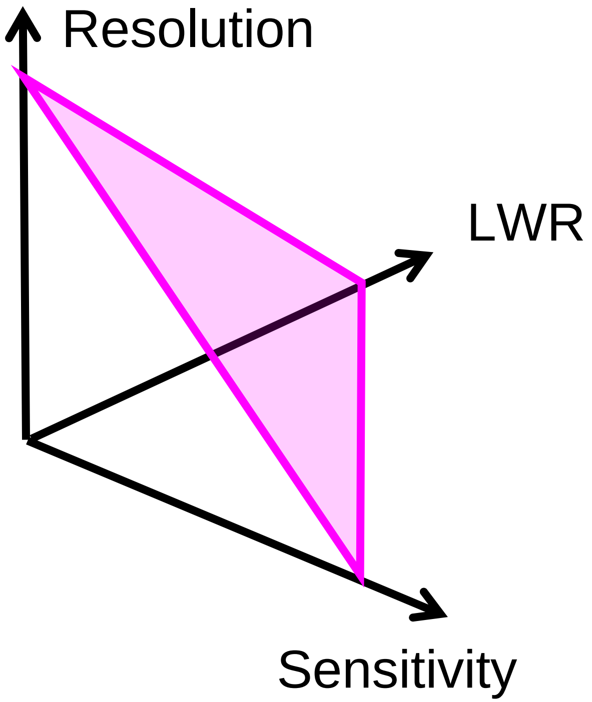
# There are two important problems in EUV resists

## (1) RLS trade off problem

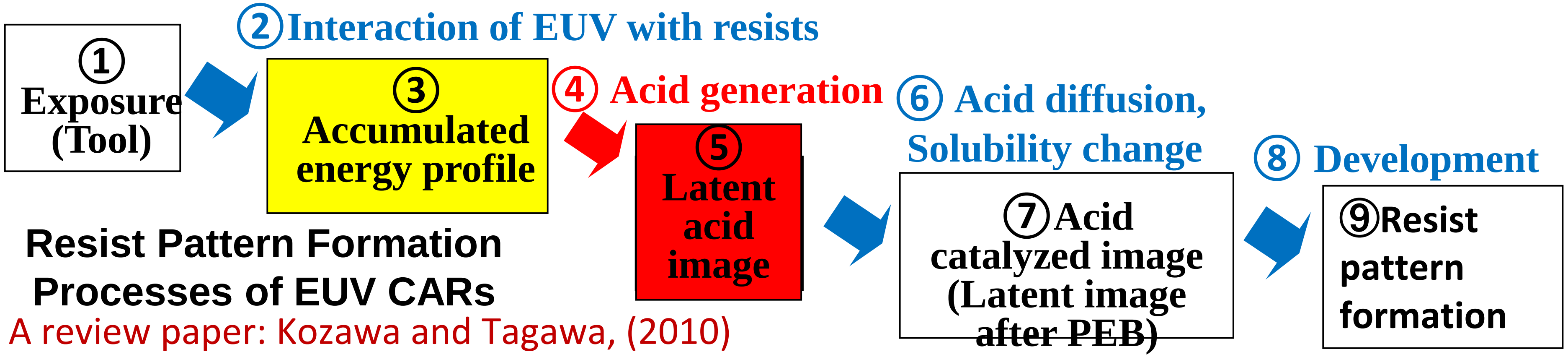
The most difficult technical requirement for EUV resist is simultaneous improvement in resolution, LWR, and sensitivity (RLS).



## (2) Photon shot noise problem

LER due to photon shot noise

# (1) RLS Trade-off Problem


①
Exposure
(Tool)

② Interaction of EUV with resists

③
Accumulated
energy profile

④ Acid generation

⑤
Latent
acid
image

⑥ Acid diffusion,
Solubility change

⑦ Acid
catalyzed image
(Latent image
after PEB)

⑧ Development

⑨ Resist
pattern
formation

**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.

**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.

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

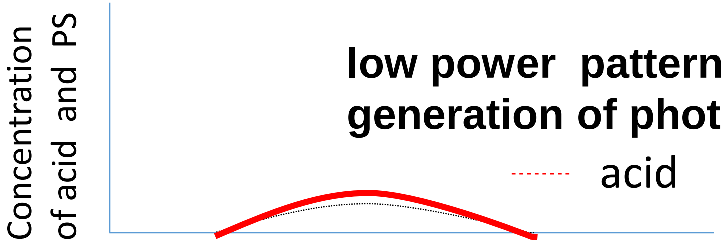
A new high resist sensitization process by the combination lithography of EUV pattern exposure with UV flood exposure of *Photosensitized Chemically Amplified Resist*™ (PSCAR™) was proposed at Osaka University in 2013. (S.Tagawa et al., J.Photoplm. Sci. Tech. 26, 825 (2013))

**CAR reactons: Pattern exposure of EUV (radiation chemistry) + thermal diffusion reaction** ➡
**PSCAR reactions: EUV Pattern exposure + UV flood exposure(photochemistry) + thermal diffusion reaction**

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

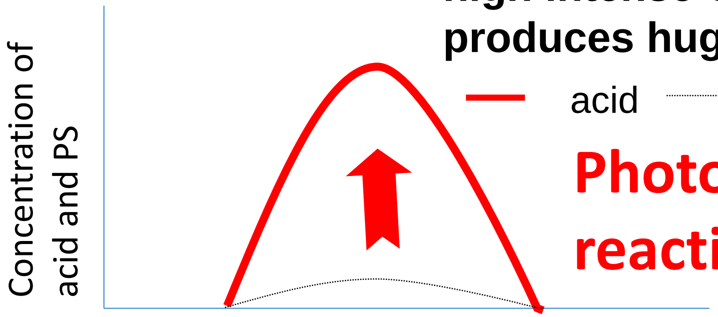
## EUV PSCAR: Combination of radiation chemistry with photochemistry

**(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**

**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.**

# PSCAR

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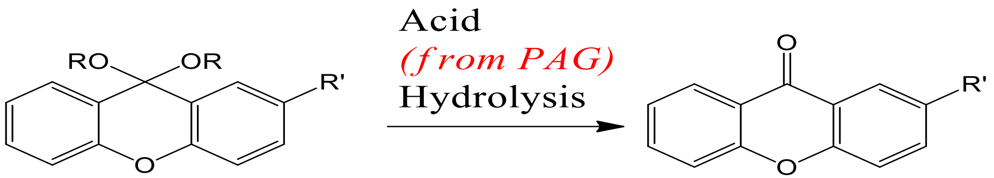
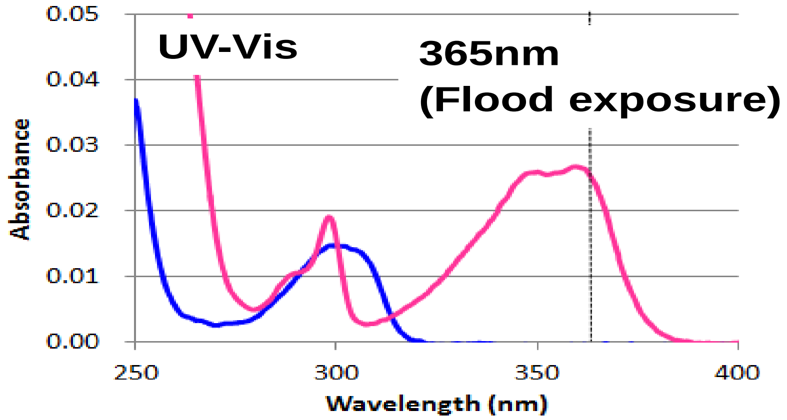
**Therefore, no reaction of resist occurs by only the second flood exposure.**
**3. Only PSs have absorption bands at the second flood exposure wavelength.**
**Sensitivity enhancement occurs by excitation of PSs.**



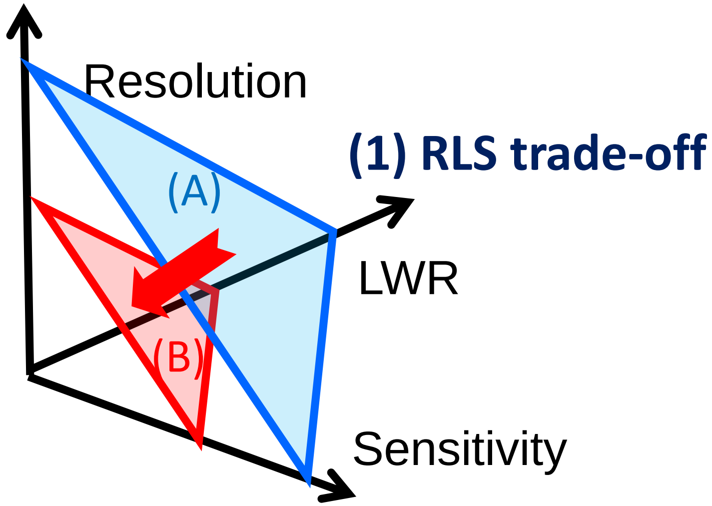
**PP-1**

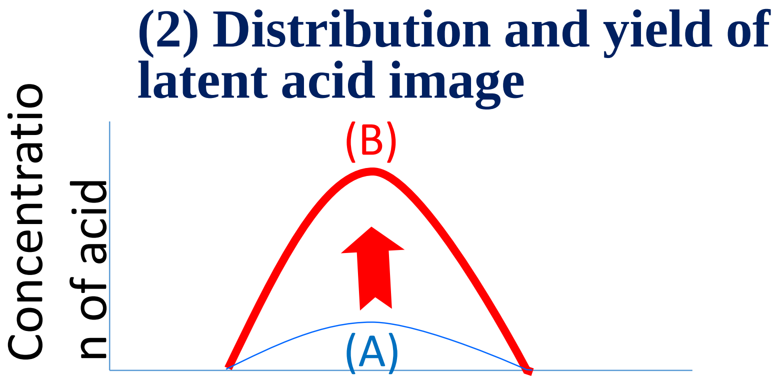
**PS**



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.

# (2) Photon Shot Noise Problem

There are so many important papers on LER due to 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)

Modified NILS (NILS*) is better for EUV/EB lithography, Kozawa and Tagawa (2009)

LER can be approximated by using chemical gradient (dm/dx) . It was experimentally confirmed.

$\mathrm{LER} = f_{\mathrm{LER}}$ (constant) /dm/dx      Kozawa, Oizumi, Itani, Tagawa (2010)

The LER originating from the fluctuation of chemical reactions increases with increasing resist sensitivity experimentally. Kozawa, Yamamoto, Tagawa (2010)

Therefore, LER due to photon shot noise can be approximated by using dm/dx for CAR.

$$\mathrm{LER}_{\text{photon shot noise}} \propto \sigma_{\text{photon shot noise}}\,(\text{constant})\,/dm/dx$$

The difference of σ(constant) and dm/dx between PSCAR and CAR?

σ(constant) depends on the distribution of acids and dm/dx depends on acids/quenchers.

# Energy Absorption Process of EUV Resists

**Interaction of EUV photon with CARs**

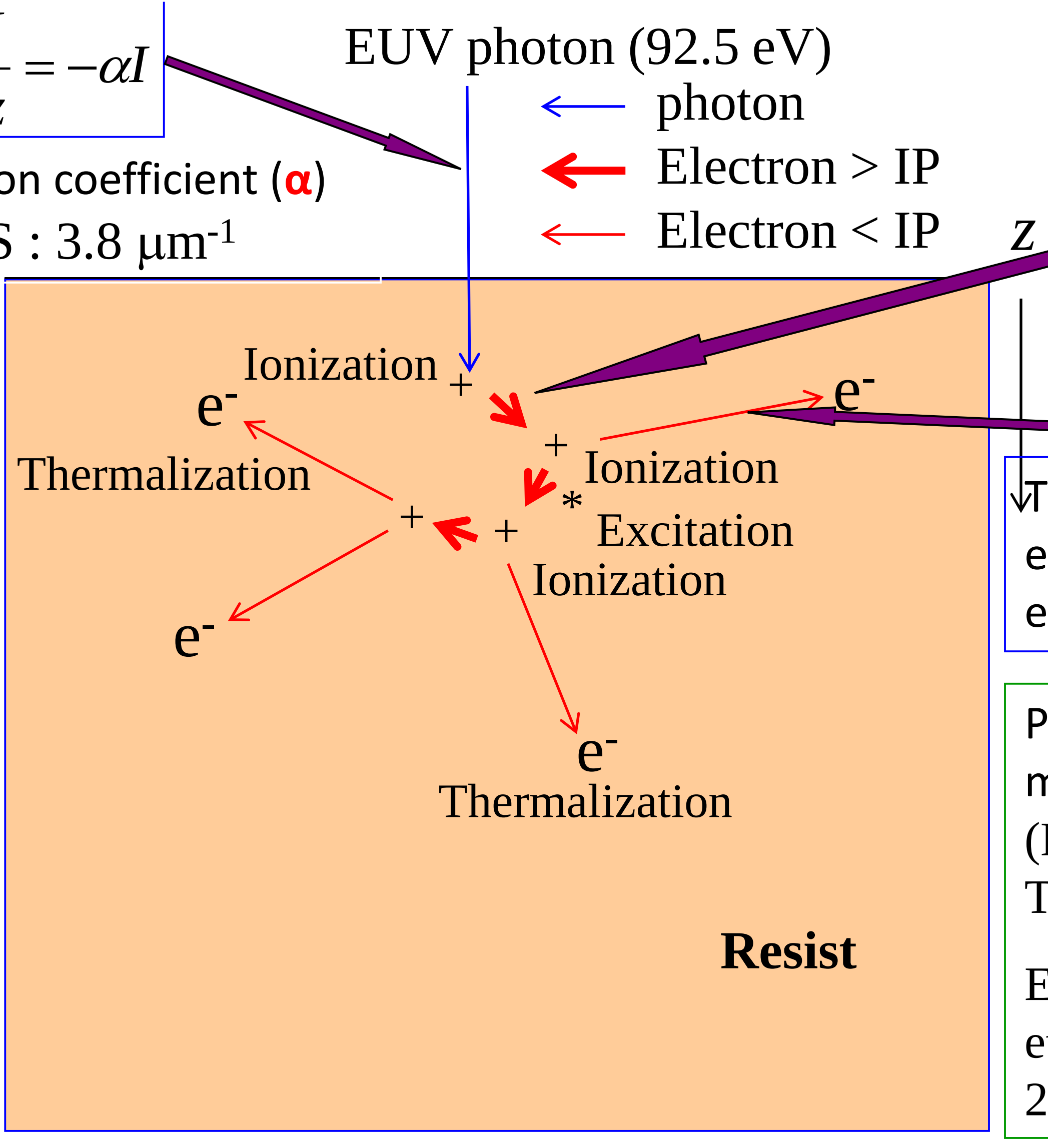
**-spatial distribution-**

Intensity of EUV ($I$)

$$\frac{\partial I}{\partial z} = -\alpha I$$

Absorption coefficient (**α**)

PHS : 3.8 μm$^{-1}$



Inelastic mean free path

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

Thermalization Length
**4.0** (3.2) nm for PHS

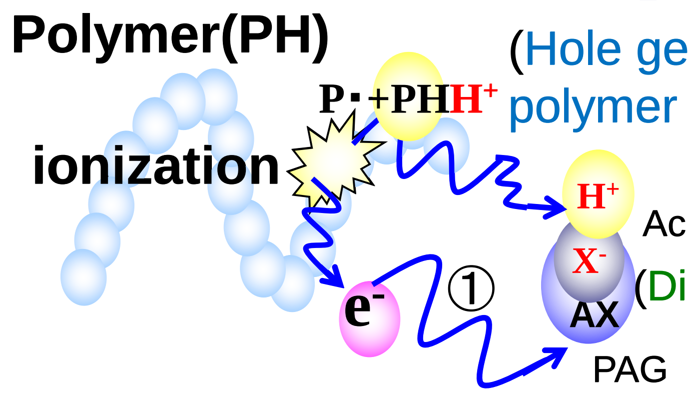
The number of secondary electrons is estimated expermentally. **4.2** for PHS

PHS with 10 wt% TPS-tf Acid molecules per photon: **2.6** (Kozawa et al. J.Vac.Sci. Tecnnol.,B25(2007) 2481)

Experimental value: **2.5** (Hirose et al.,Jap.J.Appl.Phys,Part 2(2007)

# Acid Generation of Acid (HX) in CAR

**CAR** **EUV exposure**

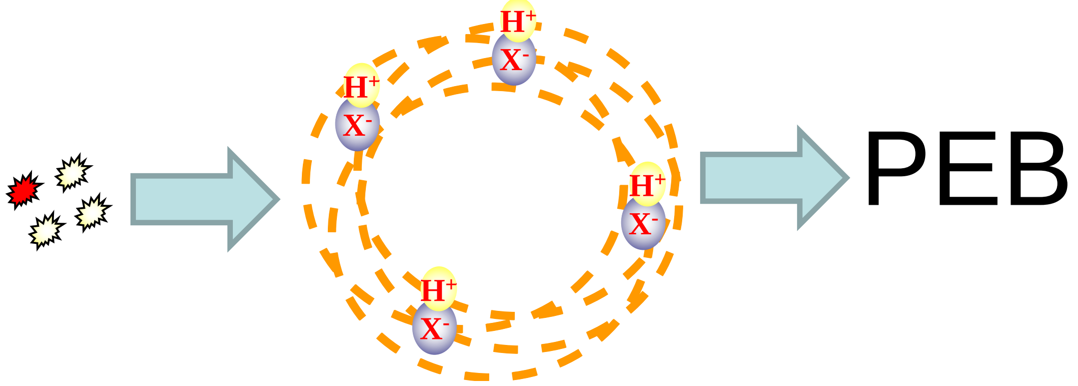


(Hole generates radical and protonated polymer by ion molecular reaction)

(Dissociative Electron Attachment)

**①Thermalization length of $e^-$ (3~4 nm for typical CAR)**

**Electron (e-) produces $X^-$ just after thermalization.**
**$X^-$ is immobile and $H^+$ is mobile in all polymers of CAR.**



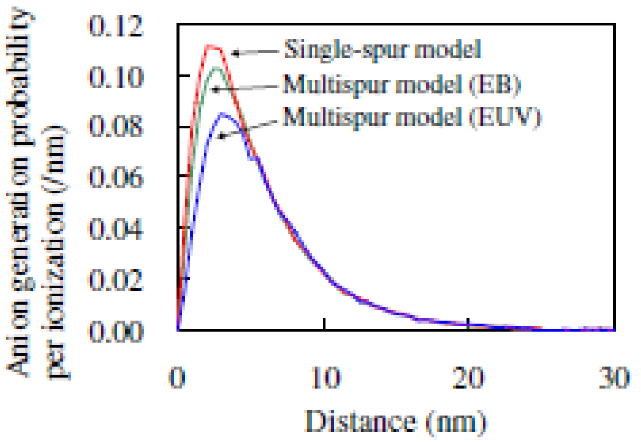


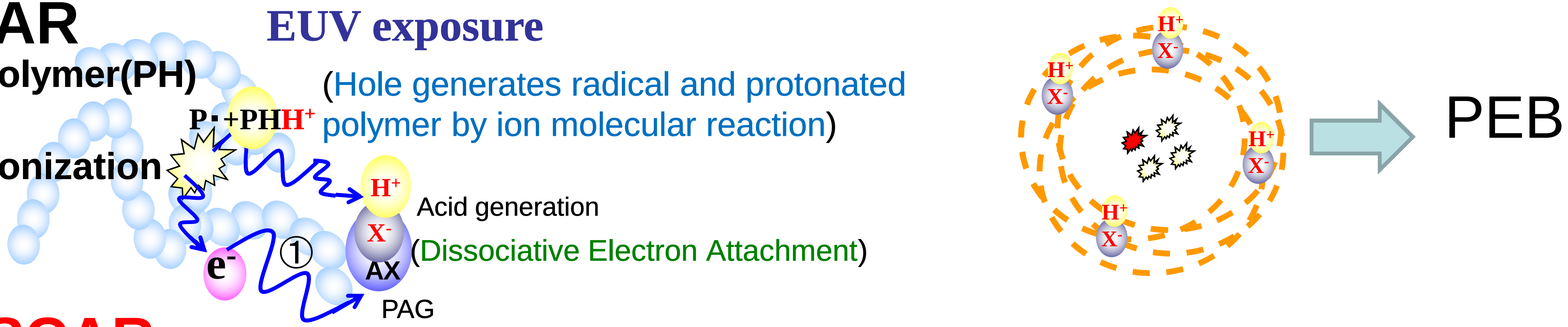
Fig. 16. (Color online) Distribution of probability of anion generation per spherical shell thickness (per ionization). The horizontal axis represents the distance from the first ionization point (the origin).[112]

Kozawa, Okamoto, Saeki, Tagawa, Jpn. J. Appl. Phys. (2009)

**Distance between ionizations > ①Thermalization length of $e^-$, Diffusion Length of Acid during PEB**

# Spherical acid cluster generation in PSCAR

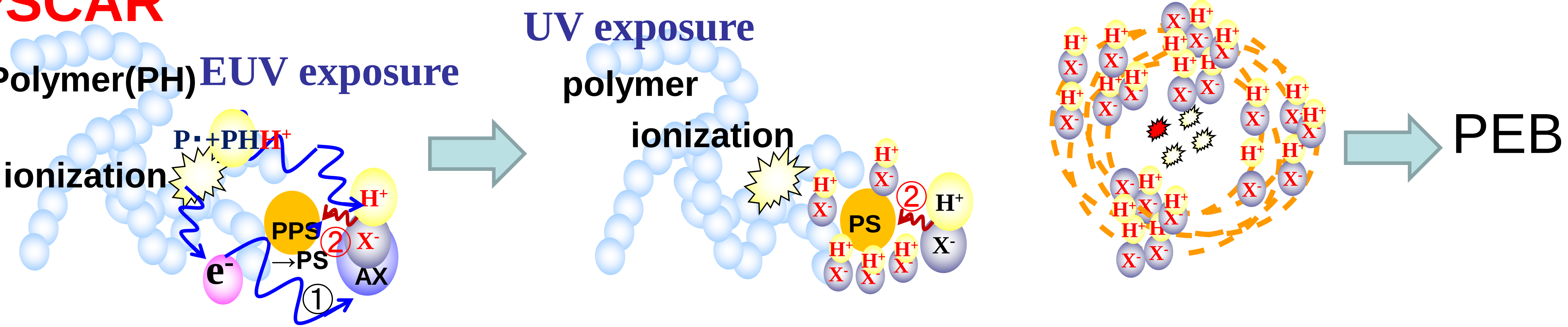
## CAR



(Hole generates radical and protonated polymer by ion molecular reaction)

(Dissociative Electron Attachment)

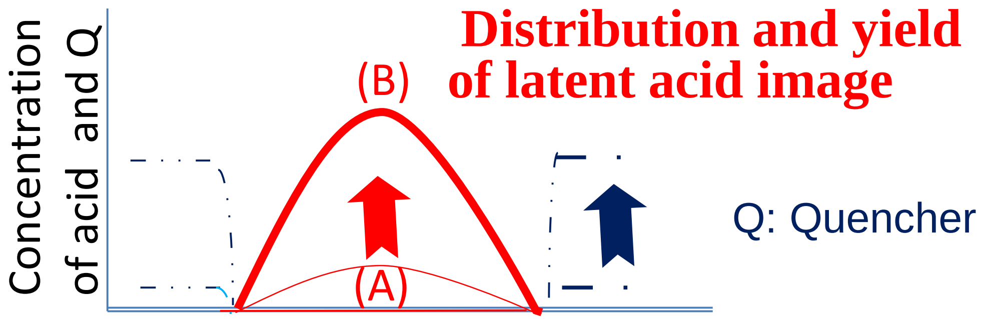
## PSCAR



**Distance between ionizations > ①Thermalization length of $e^-$ > new processes (② thermal reaction distance(at RT), Electron transfer distance from PS* to PAG) <Diffusion Length of Acid during PEB**

**In CAR and PSCAR, stochastic problem is important only around dissolution threshold area.**

# Breakthrough of Photon Shot Noise Problem



The higher concentration of quencher can be used in PSCAR than in CAR. Therefore, the higher chemical gradient (dm/dx) can be obtained in PSCAR than in CAR.

LER due to photon shot noise can be explained by using chemical gradient around dissolution threshold for both CAR/PSCAR. $\mathrm{LER}_{\text{photon shot noise}} \propto \sigma_{\text{photon shot noise}}/dm/dx$

**CAR**

EUV Pattern exposure + thermal reaction

Acid generation(AG) ⇨

acid catalyzed reaction (PEB)

⇨

***PSCAR***$^{\text{TM}}$

(EUV Pattern + UV flood) exposure + thermal reaction

AG + PS generation ⇨

**spherical acid cluster generation** ⇨ PEB

# Conclusion

- PSCAR is good solution for breakthrough of both RLS trade-off and photon shot noise problems.
- 125 keV EB exposure experiments at Osaka University showed very good results for PSCAR.
- Now collaboration partner companies have been examined PSCAR performance with the different types of PSCAR materials by simulation and EUV exposure experiments. Further optimization of PSCAR material formulation is needed but the initial results by preliminary off-line flood exposure experiments on ASML NXE:3300 at imec with TEL's standalone pre-alpha flood exposure tool are promising to understand the possibility of PSCARs.
- Improvement of optimization of processes, materials, and systems for PSCAR is always important, but improvement of PSCAR proceeds steadily and much faster than CAR. EUV CARs have been improved now very slowly but steadily by worldwide efforts based on the resist pattern formation model of EUV CARs including radiation chemistry even after 35 years since the birth of CAR in IBM.

# Acknowledgments

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