

Optimizing RLS

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IEUVI Resist TWG
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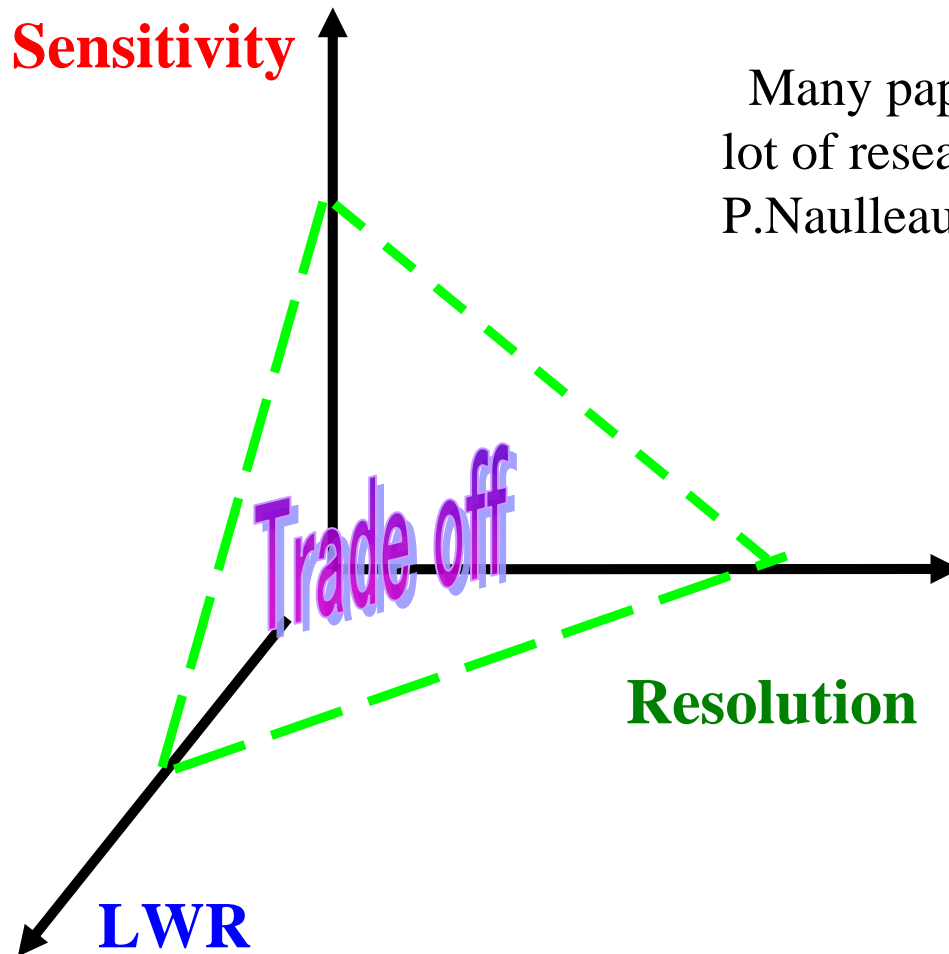
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RLS Trade Off:

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.Nauleau, G.Gallatin, et al.

Experiments

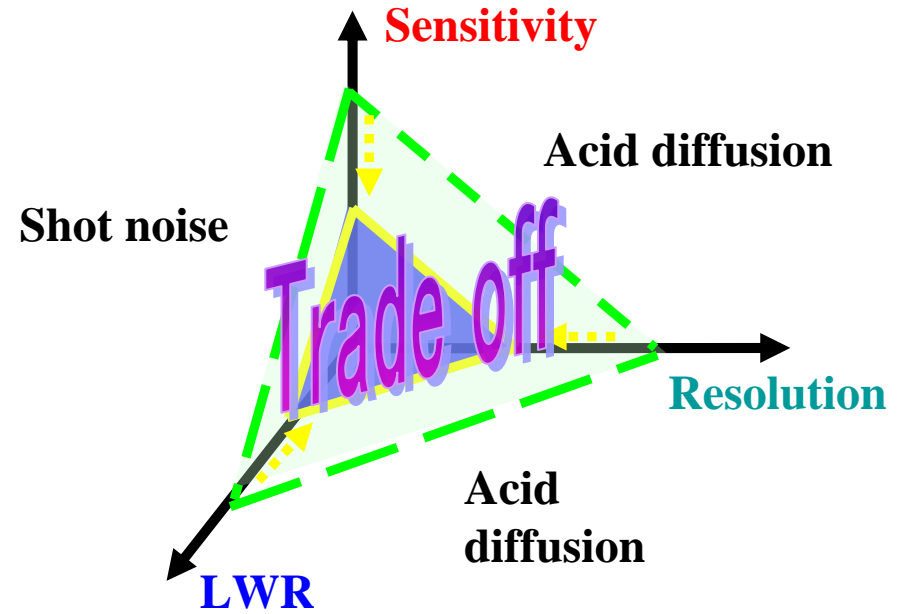
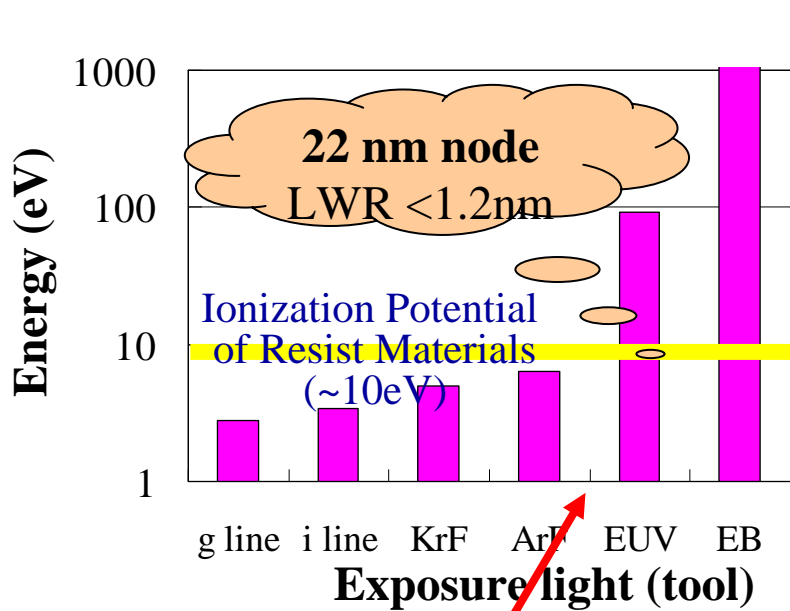
R.Brainard et al. SPIE(2004)

P.Nauleau et al. SPIE(2006)

Simulations

G.M.Gallatin, SPIE(2005)

How to optimize RLS: Fundamental research is essential.

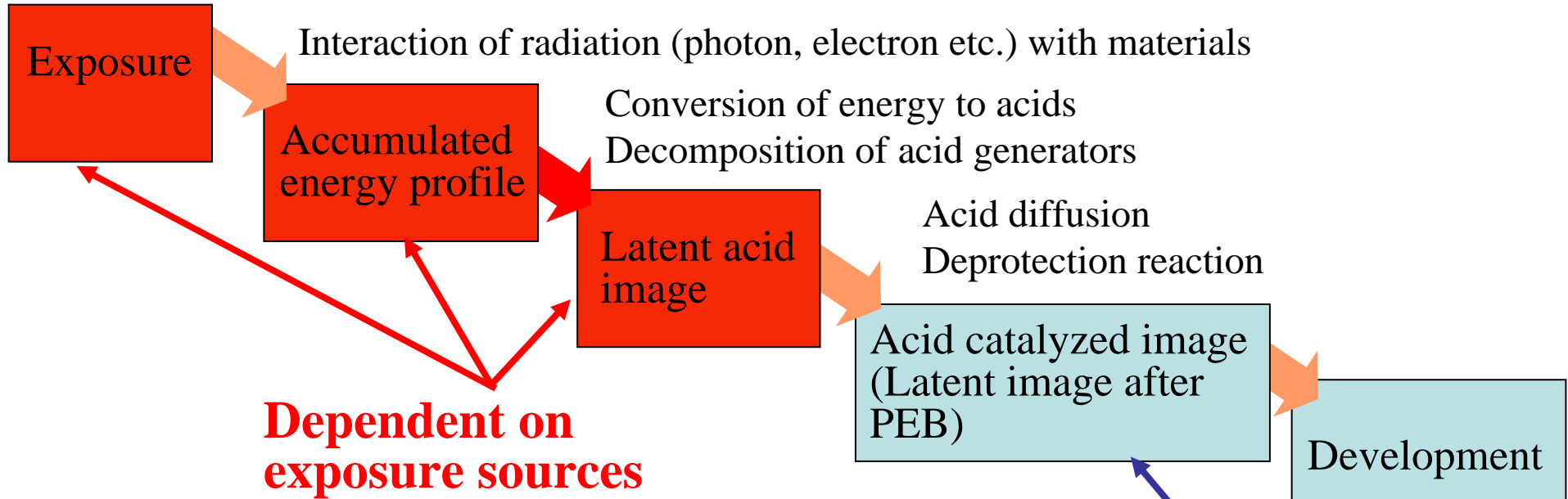


Huge amounts of knowledge infrastructure based on photochemistry are available for photoresists.

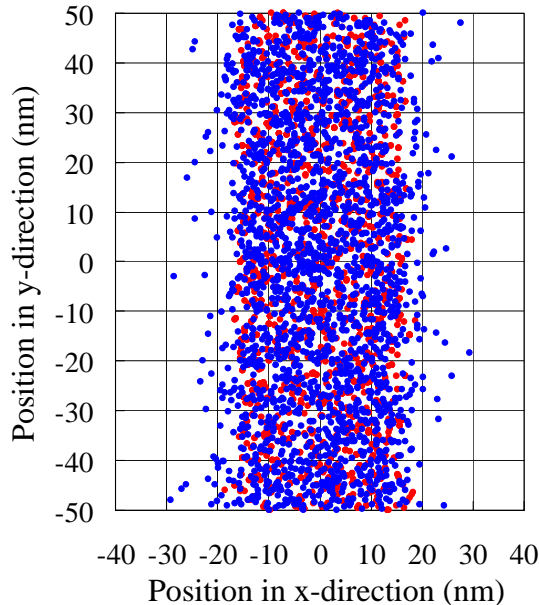
Solutions!
One of the best solution is the increase in pattern formation efficiency

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

Resist pattern formation processes



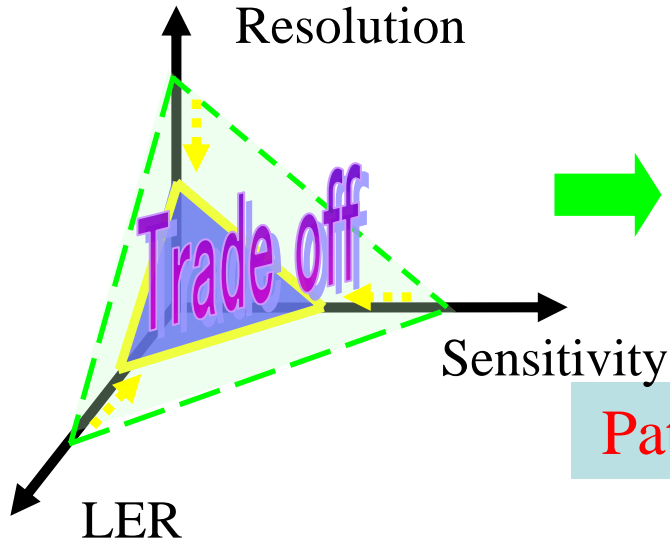
Dependent on exposure sources



- Proton
- Anion

Proton-anion distribution

Independent of exposure sources



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

Pattern formation efficiency

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

Exposure source dependent

X

Limited by side wall degradation

Quantum yield of acid

Exposure source independent

X

Limited by secondary electron emission efficiency

Efficiency of catalytic chain reaction

Limited by diffusion-controlled rate for chemical reaction

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

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

Acid diffusion and reaction

$$\frac{\partial u_{acid}}{\partial t} = \nabla(D_{acid} \nabla u_{acid}) - k u_{acid} u_{quencher}$$

Base quencher diffusion and reaction

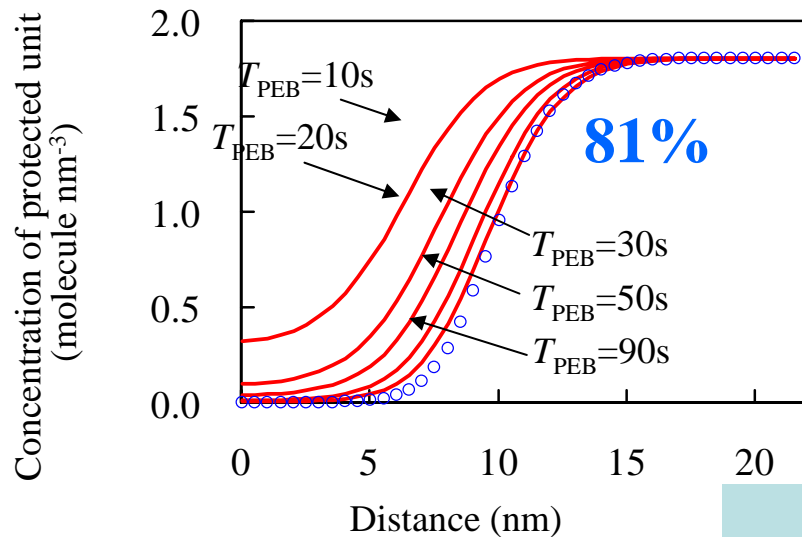
$$\frac{\partial u_{quencher}}{\partial t} = \nabla(D_{quencher} \nabla u_{quencher}) - k u_{acid} u_{quencher}$$

Deprotection reaction, especially rate constant

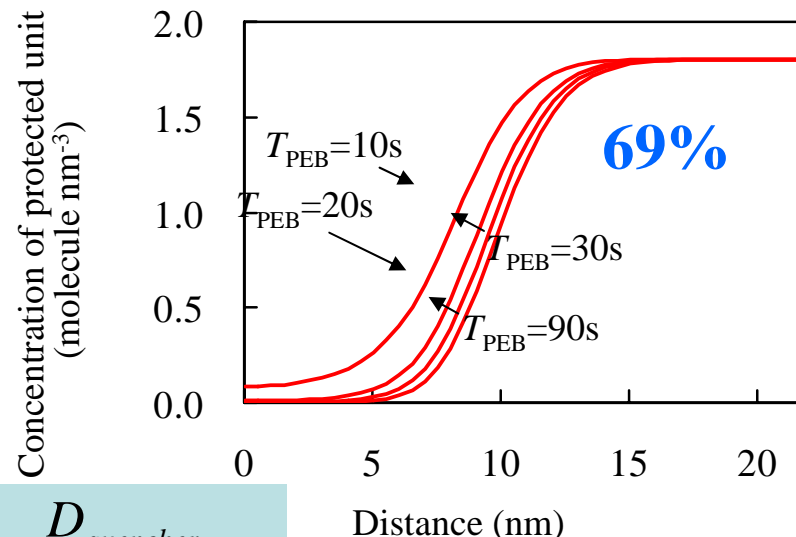
$$[P] = -\int_0^{T_{PEB}} k_{depro} u_{acid} [P] dt$$

Optimization of quencher concentration for each α

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

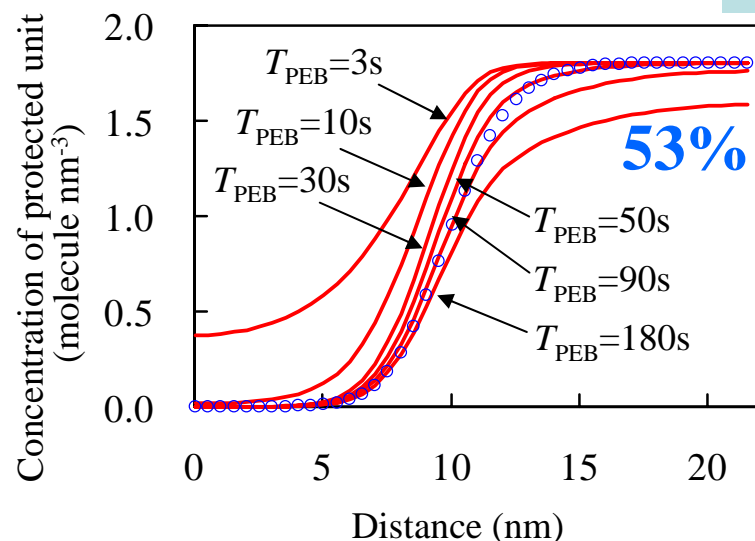


(a) $\alpha = 0.1$



(b) $\alpha = 1$

$$\alpha = \frac{D_{quencher}}{D_{acid}}$$



(c) $\alpha = 10$

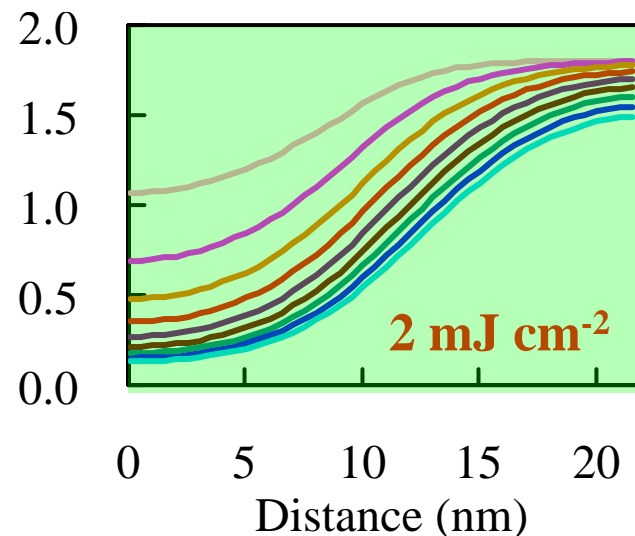
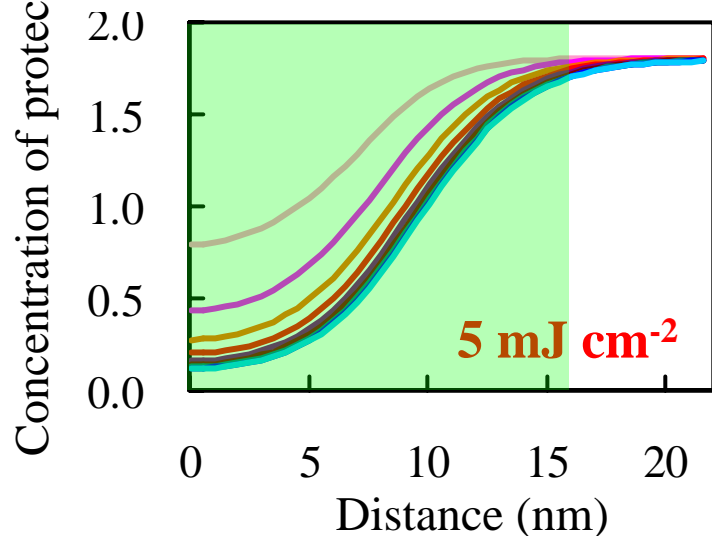
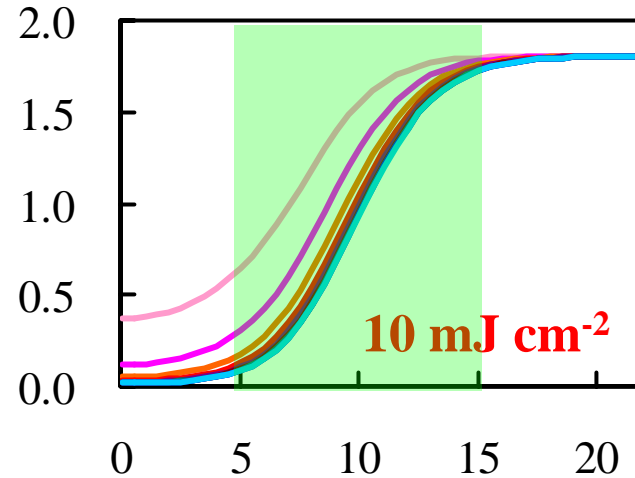
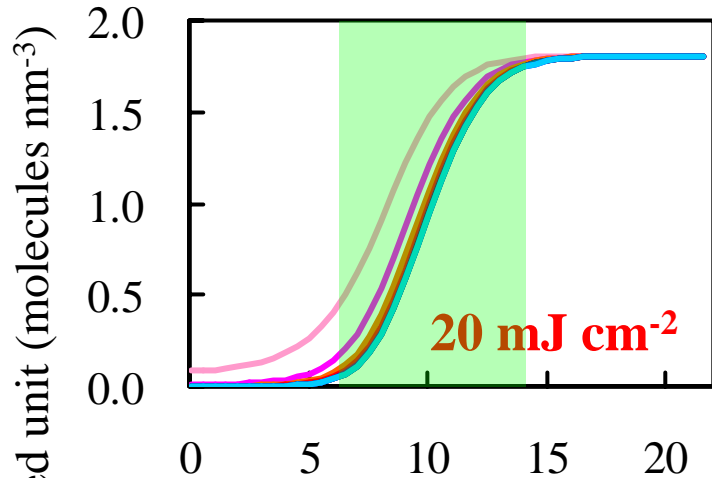
Fig. Temporal changes of latent images during PEB. The exposure dose is 20 mJ cm^{-2} . The quencher concentrations are (a) 81%, (b) 69%, and (c) 53% of initial acid concentration at the origin. The open circles represent the same deprotection profile as the one at $T_{PEB} = 90 \text{ s}$ in Fig. (b).

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

Limit of PHS-based chemically amplified resist

Jpn. J. Appl. Phys. 47 (2008) 4465.

Latent images of 22 nm line & space



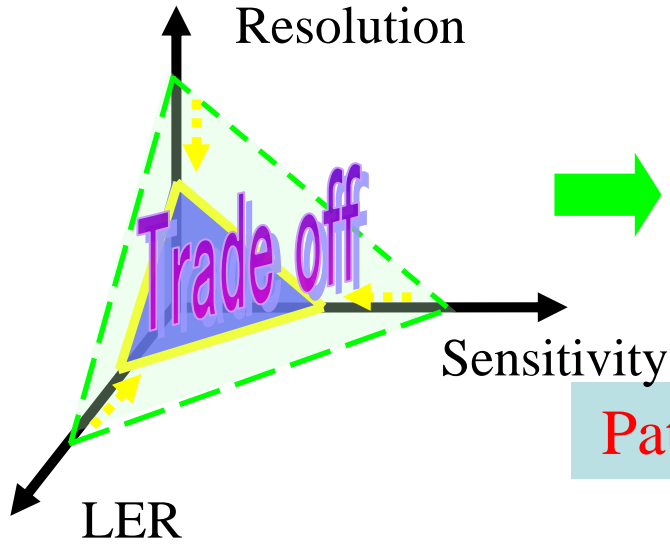
Intermediate region where protected and deprotected units coexist

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.

Some special consideration such as anisotropic acid diffusion (Gallatin, Naulleau, Brainard SPIE(2007)) and nonconstant diffusion coefficient. (T. Kozawa et al., J. Photopoly.Sci.Tech., 21(2008)421)



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

Pattern formation efficiency

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

Exposure source dependent

X

Limited by side wall degradation

Quantum yield of acid

Exposure source independent

X

Limited by secondary electron emission efficiency

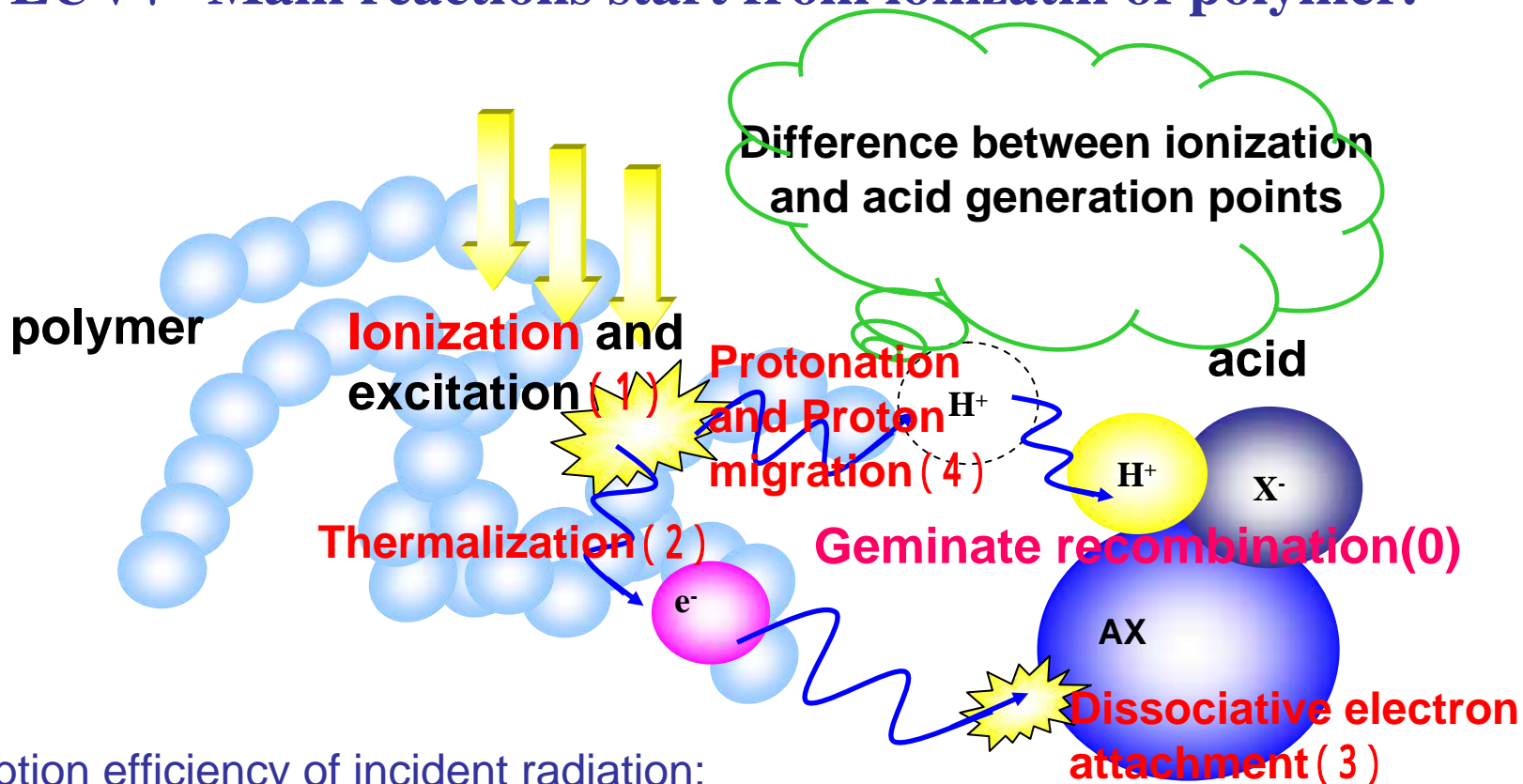
Efficiency of catalytic chain reaction

Limited by diffusion-controlled rate for chemical reaction

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

Acid Generation of Chemically Amplified EUV Resists

EUUV: Main reactions start from ionization of polymer.



Absorption efficiency of incident radiation:

absorption coefficient, 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:

reaction of epithermal electrons (K. Natsuda et al. J.J.Appl.Phys., 47(2008)4932)

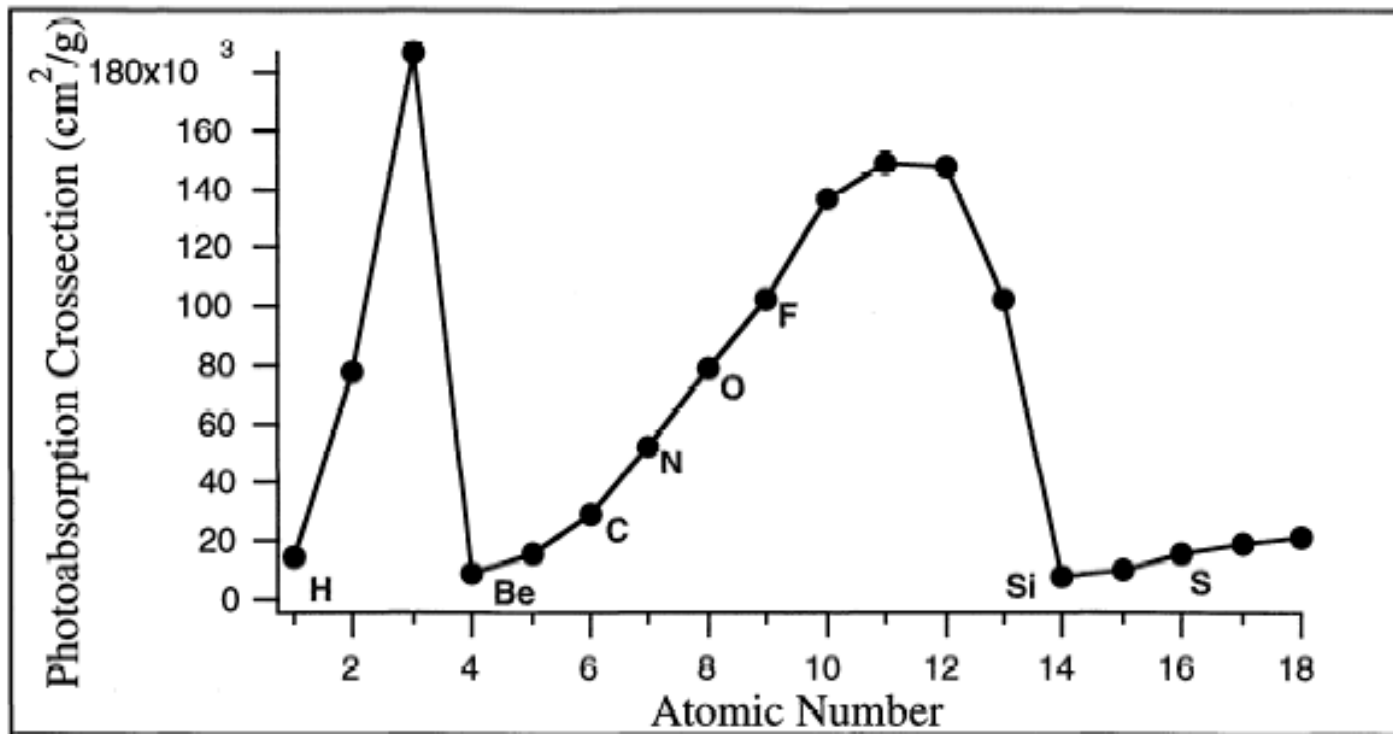


Figure 1: Elemental absorption cross-sections at 13.4 nm wavelength. Elements commonly found in photoresist materials are H, C, N, O, F, and S.

Interaction of EUV photon with CARs

-spatial distribution-

Intensity of EUV (I)

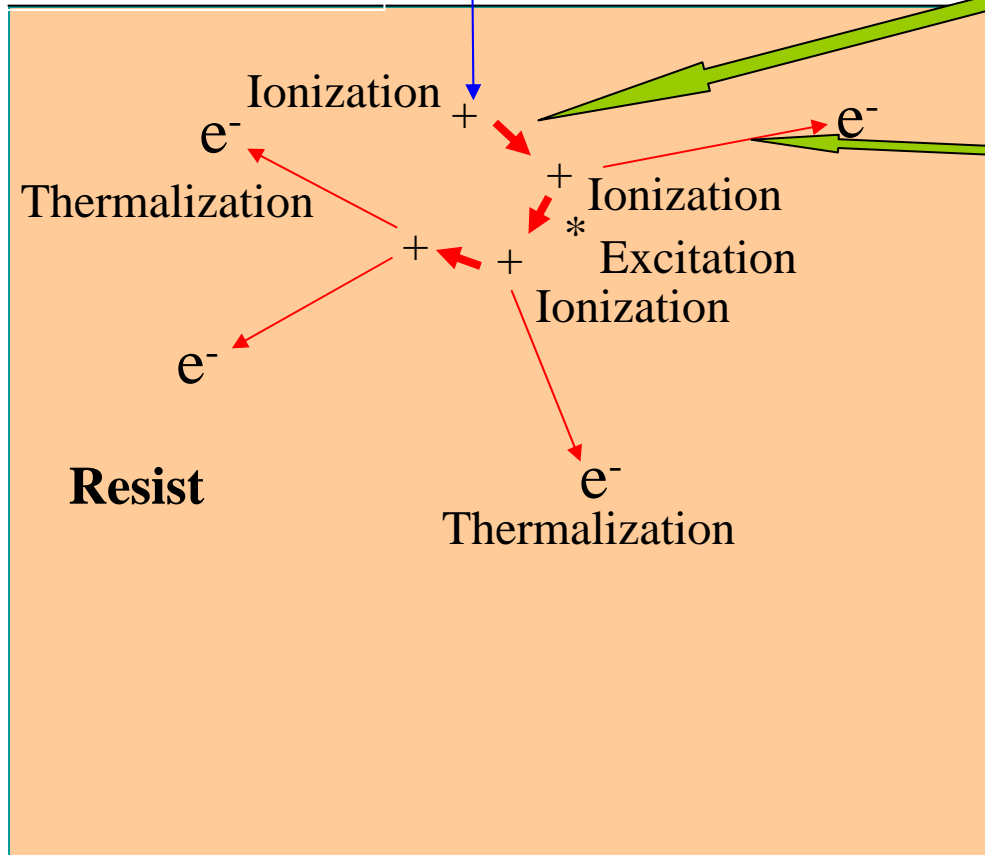
$$\frac{\partial I}{\partial z} = -\alpha I$$

EUV photon

- ← photon
- ← Electron > IP
- ← Electron < IP

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

Absorption coefficient ()
 PHS : $3.8 \mu\text{m}^{-1}$



Thermalization Length
4.0 nm for PHS

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

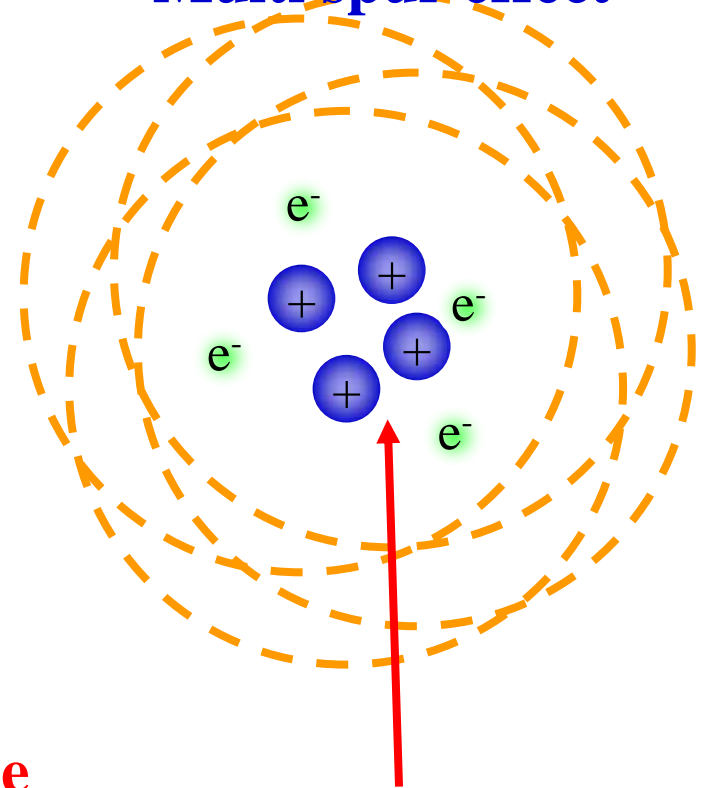
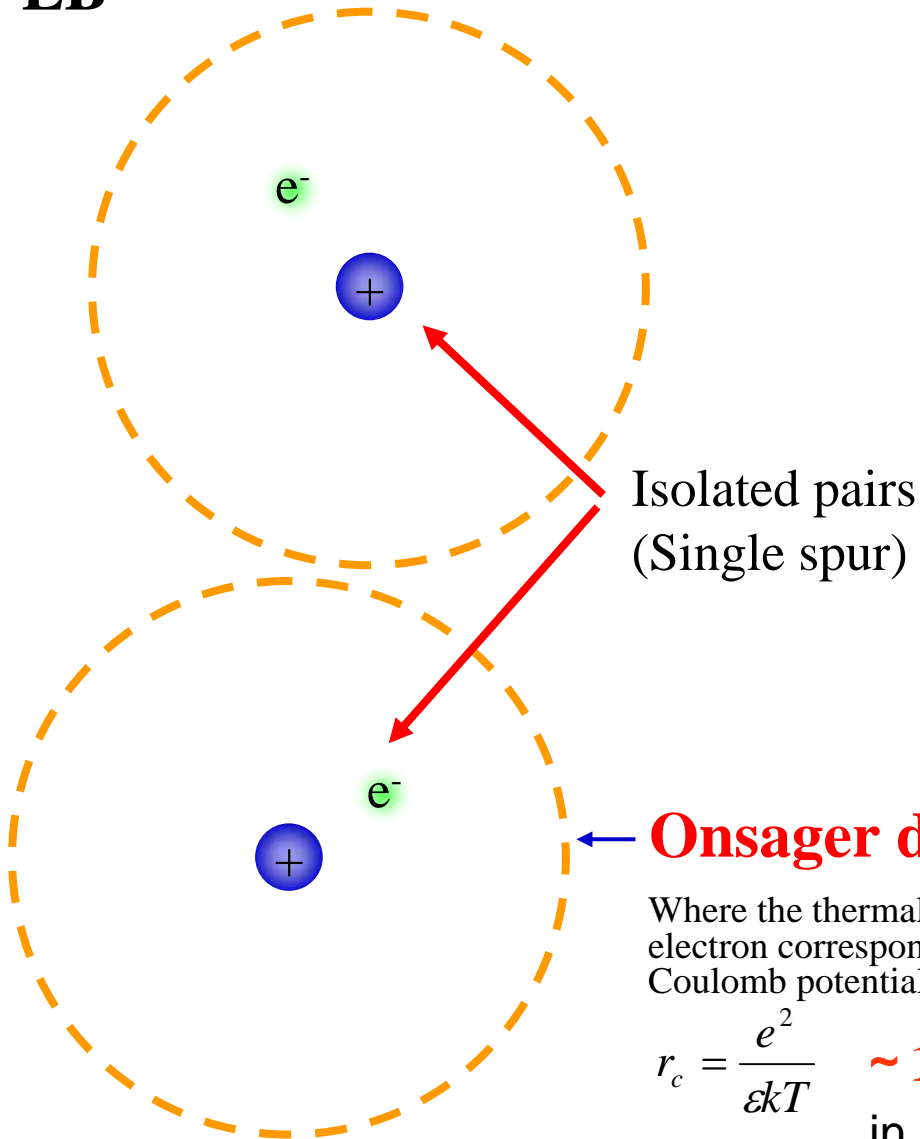
PHS with 10 wt% TPS-tf Acid molecules per photon: 2.6 (Kozawa et al. J.Vac.Sci. Tecnnol.,B25(2007) 2481)
 Experimental value: 2.5 (Hirose et al.,Jap.J.Appl.Phys,Part 2(2007))

Difference between EB and EUV

EB

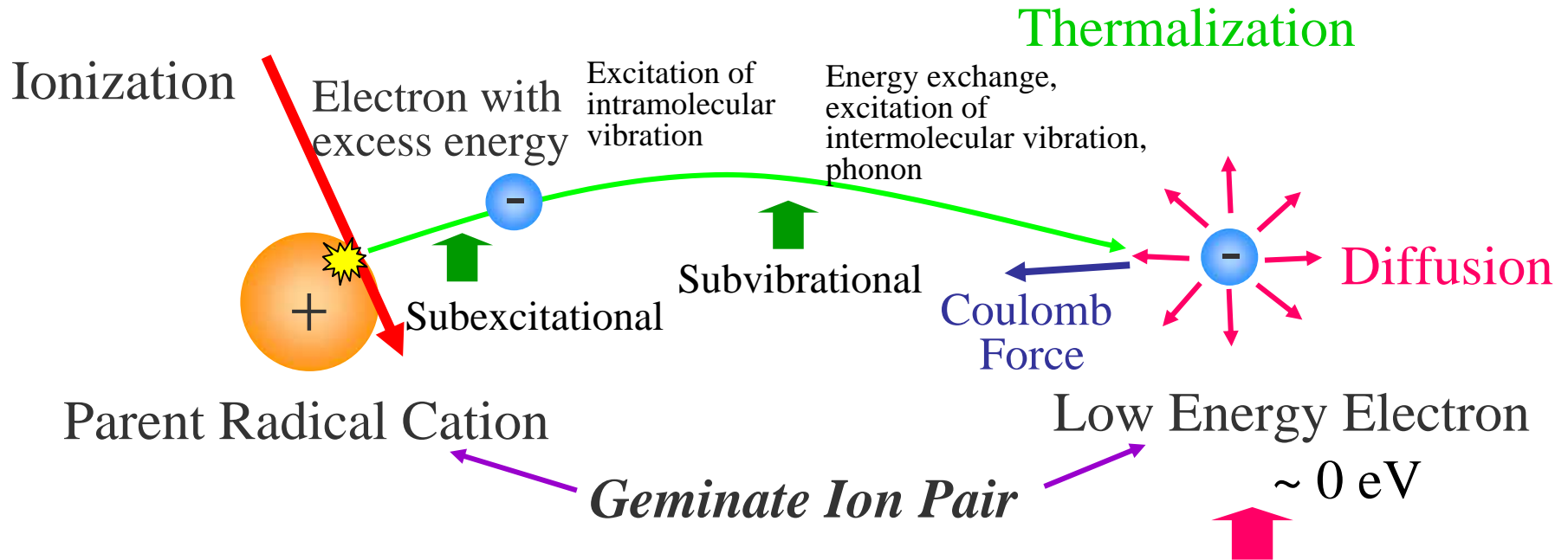
EUV

Multi spur effect



(Kozawa et al., J.Appl.Phys, 103(2008)84306)

Electron dynamics in early processes of radiation chemistry



Acid generator can react with these low energy electrons.

Modified Smoluchowski equation for CAR

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

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**

Difference in sensitization distance between EUV and EB

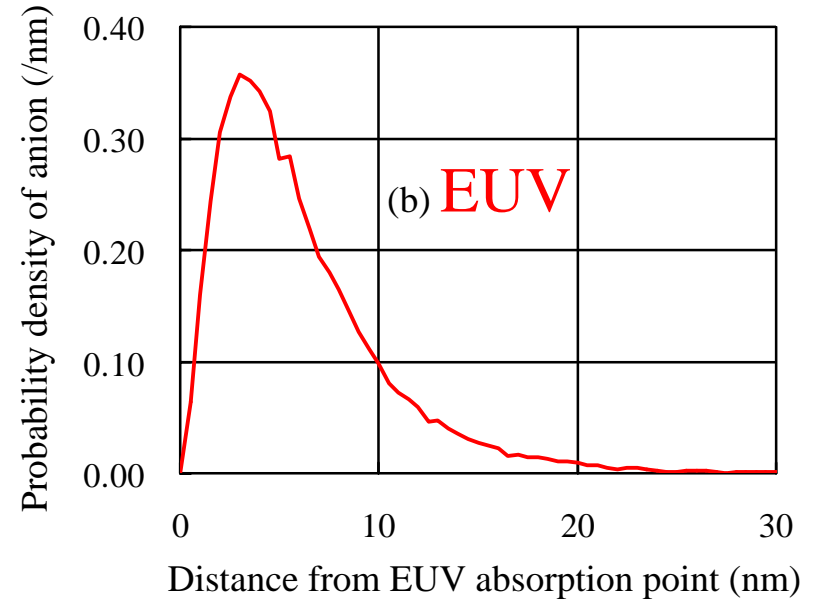
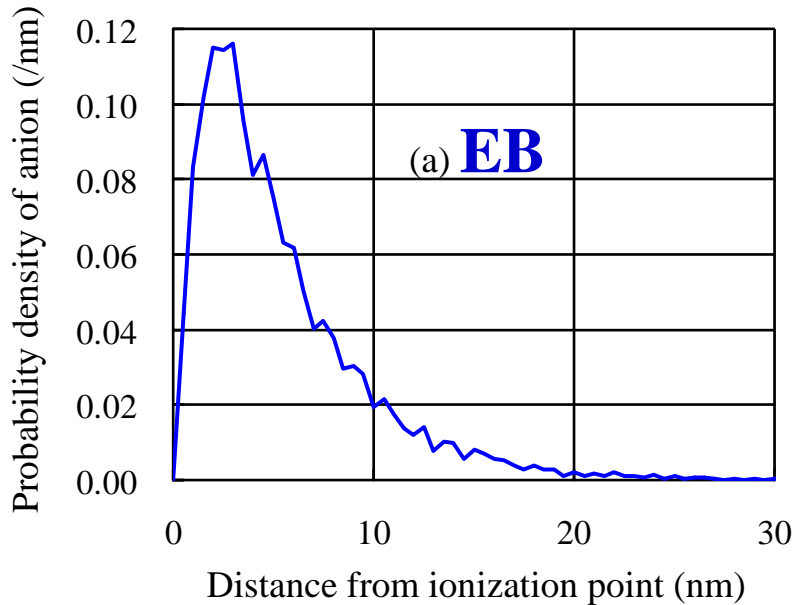


Fig. Probability density of anion generated in PHS with 10 wt% TPS-tf by (a) an electron and (b) an EUV photon.

Sensitization distance (ionization)

5.6 nm

6.3 nm

Acid generation efficiency (ionization)

0.74 per ionization

0.62 per ionization

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

2.6 acids per one photon(92.5 eV) in PHS

Kozawa et al. J.Vac.Sci.Tecnnol.
B24,3055(2006)

Kozawa and Tagawa, J.Vac.Sci.Tecnnol.,B25(2007) 2481

Experimental value: **2.5** Hirose et al., Jap.J.Appl. Phys, Part
2 Let. & Express Let.,46,L979(2007)

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

(Appl. Phys. Express 1(2008)47001, 67012)

Current status

Sensitivity : 10~20 mJ cm⁻²

Abs. coefficient : 3.8 μm⁻¹ (PHS)

Thickness : 50 nm (40-75 nm)

Transparency : 83%

X 1/4

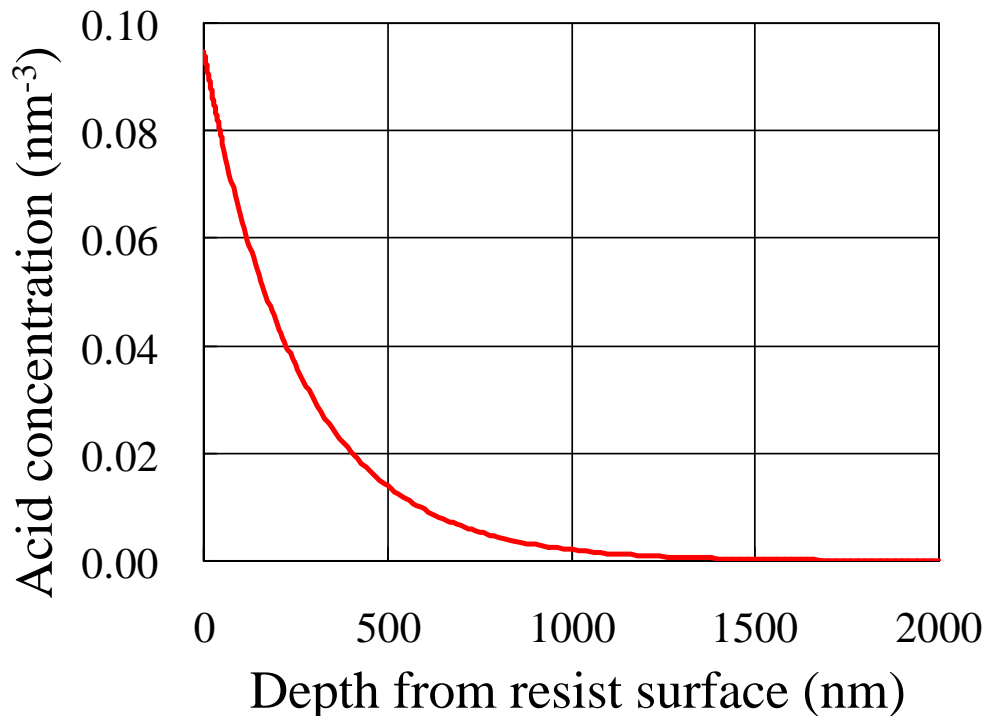


Sensitivity : <5 mJ cm⁻²

Abs. coefficient : 16 μm⁻¹

Thickness : 20 nm

Transparency : 73%



Depth profile

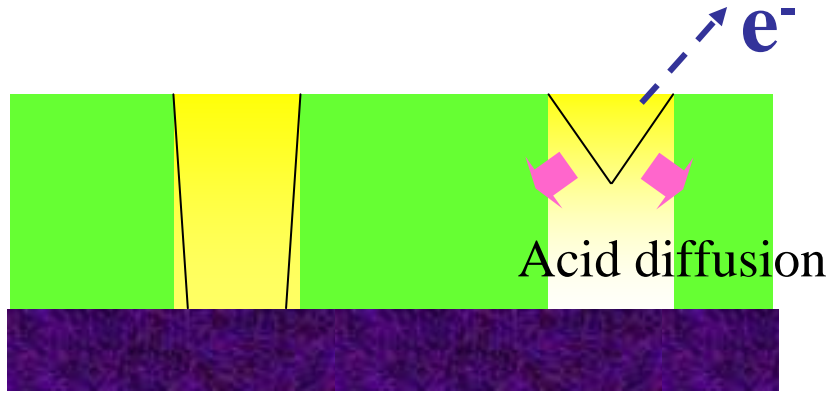
Fig. Depth profile of acid concentration (The number of acid molecules per unit volume). The exposure dose is 10 mJ cm⁻².

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.

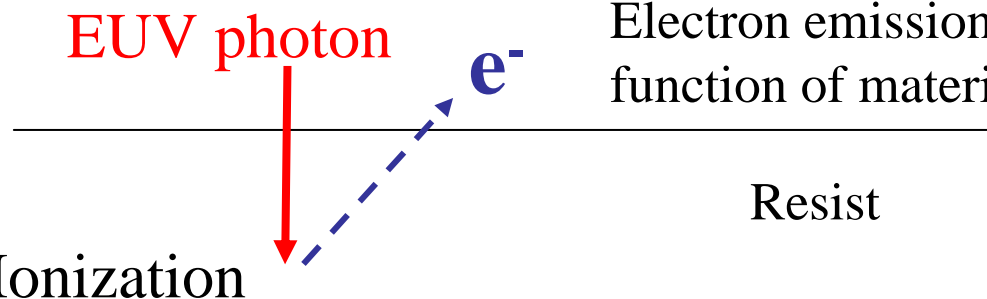


Moderation through acid diffusion



Restriction in acid diffusion + Effect of secondary electrons

Electron emission from surface



Electron emission depends on work function of materials, W_f .

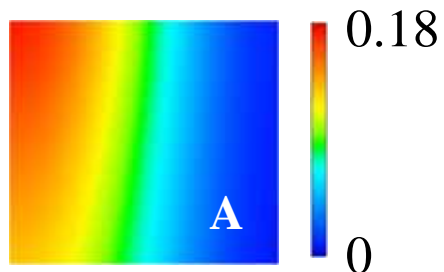
Resist

Total-reflection model: $W_f =$

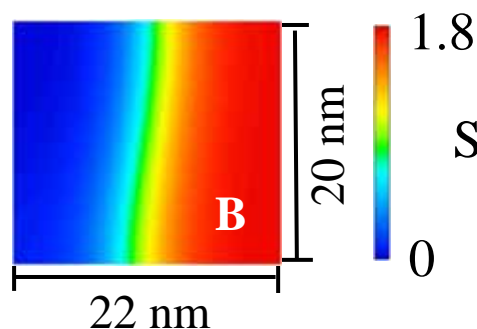
Total-transmission model: $W_f = 0$

22 nm L&S image formed in high absorption resist upon 5 mJ cm⁻² exposure

Initial acid image

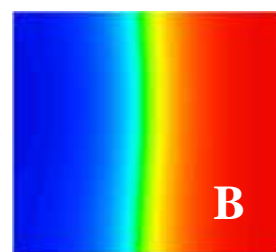
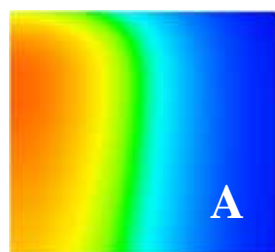


Latent image



Side wall angle: 84.5 °

(a) Total-reflection model



Side wall angle: 89.4 °

(b) Total-transmission model

Two-dimensional initial acid distribution (A) and latent image (B) of 22 nm line-and-space patterns, calculated using $a = 16 \mu\text{m}^{-1}$ with (a) total reflection and (b) total transmission models. The film thickness is 20 nm. The exposure dose is 5 mJ cm⁻². The quencher concentration is optimized to be 55% of the initial average acid yield in an area with the peak EUV intensity.

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.