Radiation Chemistry of EUV and EB Resists

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Importance of Nanospace Radiation Chemstry in EUV and EB Resist Development

- Development of high sensitive resists with enough resolution and LER is important target, because the sensitivity of resists and the intensity of exposure dose are complementary. Huge amount of development and running costs of exposure systems decrease with increasing the resist sensitivity.
- It is important to make clear the origin and the solution of RLS (resolution, LER and sensitivity) trade-off problem.
- The reduction of LER is the most serious problem in EUV resist development near future. The more detailed research on nanospace reactions and molecular interactions in EUV and EB resists is necessary in the future.

1. The relation between RLS trade-off and radiation chemistry
2. The importance of nanospace radiation chemistry in resist pattern formation in EUV and EB resists.

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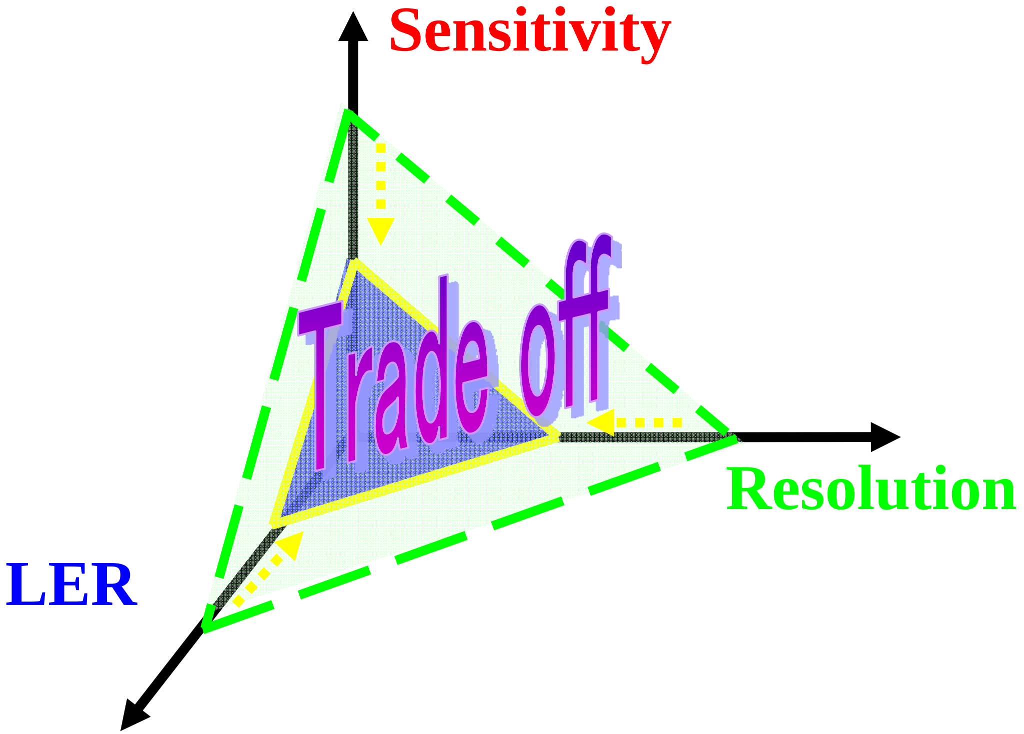
EUV resist net conference menbers of URVIC (University, Research Institute, Venture Company, Industry, Consortia) net (Chairman) Discussion about EUV resist materials & processes: many researchers in universities, industries and research consortia, espescially Selete members (Dr. H. Watanabe, Dr. Mori, Dr. Itani), Profs (T. Nishikubo, Ueda, Shirai, Kozawa), Industry attendants.

What is RLS Trade-off Problem

Many researchers had arrived at the RLS (R*esolution*, LER, Sensitivity) trade-off triangle around 2003. Resist development almost stopped several years.



What is the Origin of RLS Trade-off Problem

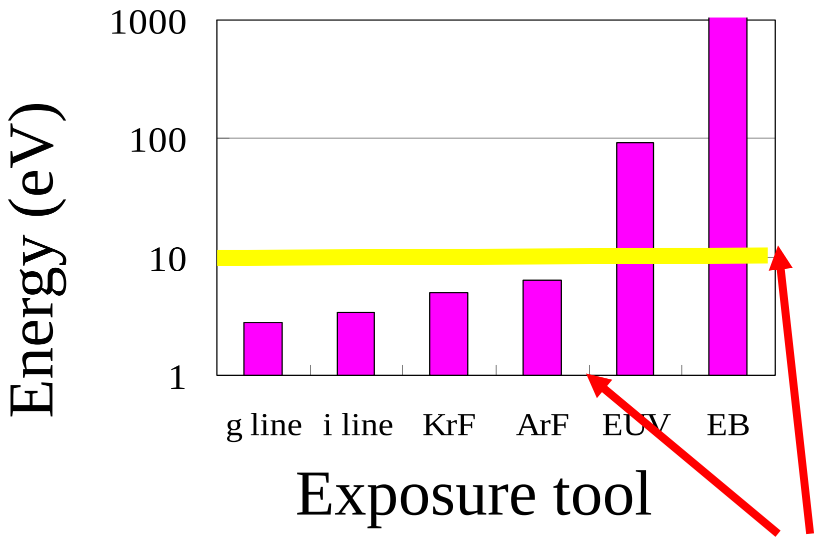
Chemically amplified resists (CARs) with high concentration of quenchers

- 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 requred less than 40 nm resolution. So RLS trade-off appeared in EUV resist research at first.

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

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.

Ionization Potential of Resist Materials (~10eV)

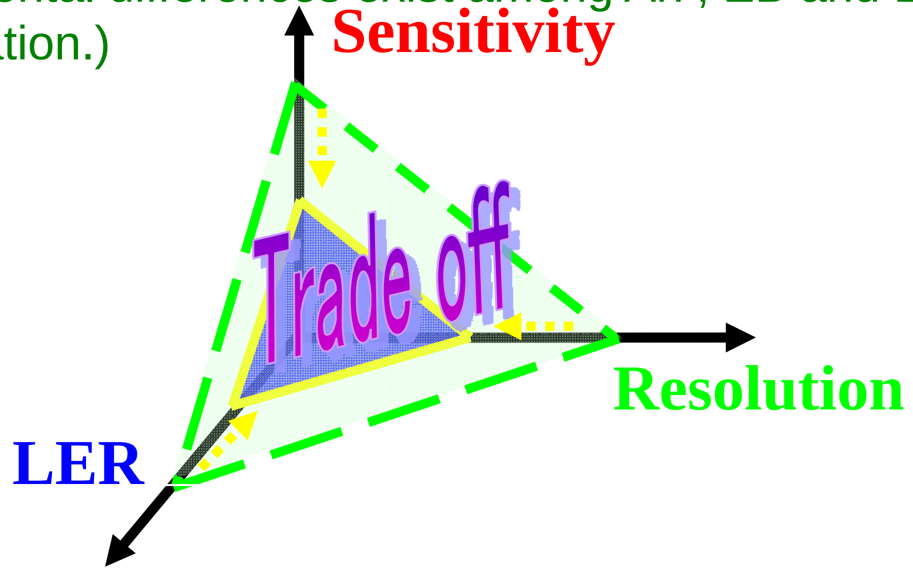
RLS Trade-off Problem

Most researchers had arrived at the RLS trade-off triangle.

Many experimental results: For example, *Brainard et al., Proc. SPIE (2004), Pawloski et al., Proc. SPIE (2004), Wallow et al., Proc. SPIE (2008)*

Simulations: *G.M. Gallatin, Proc. SPIE (2005) , D. Van Steenwinckel et al., Proc. SPIE (2007), R.L. Bristol, Proc. SPIE (2007)* (Simulations do not contain EUV -induced acid generation mechanism: No fundamental differences exist among ArF, EB and EUV resists after latent acid image formation.)

RLS trade-off is not specific.



Two questions

(1) Are acid formation mechanisms of EUV resists important in resist development? Yes, it is very important.

(2) Why such high concentration quenchers cannot scavenge acid before chemically amplified reactions occur? There are two reactions for acid generation, bulk and geminate reations.

Quencher Effects on Acid Generation of EB & EUV CARs

- EUV and EB resists (Main acid generation processes)

$RH \rightsquigarrow RH^{+\cdot} + e^-$ (Ionization + Electron Generation)

$RH^{+\cdot} + RH \rightarrow R^{\cdot} + RHH^+$ (Protonated Molecule Generation)

$Ph_3S^+X^- \xrightarrow{e^-} Ph_2S + Ph^{\cdot} + X^-$ (Dissociative Electron Attachment)

$H^{\cdot+} + X^- \rightarrow H^+X^-$. (Acid Generation by Mainly Geminate Ion Recombination)

+ Quenchers

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

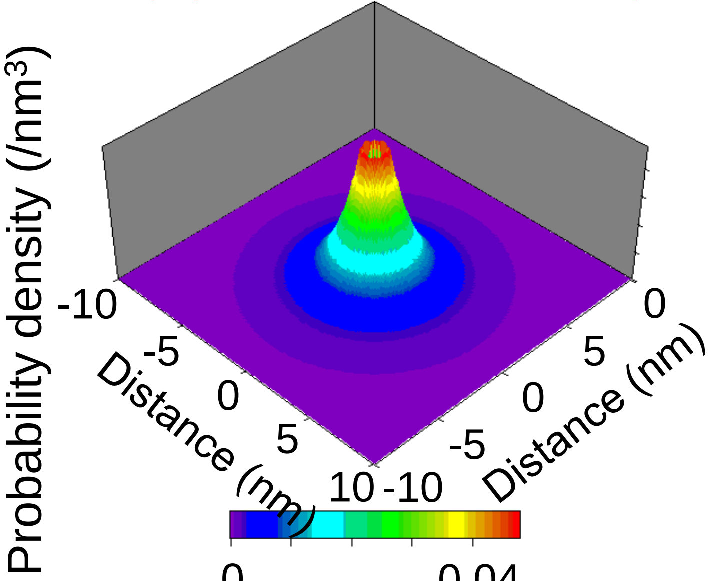
Competition reactions

$H^+ + Q \rightarrow QH^+$

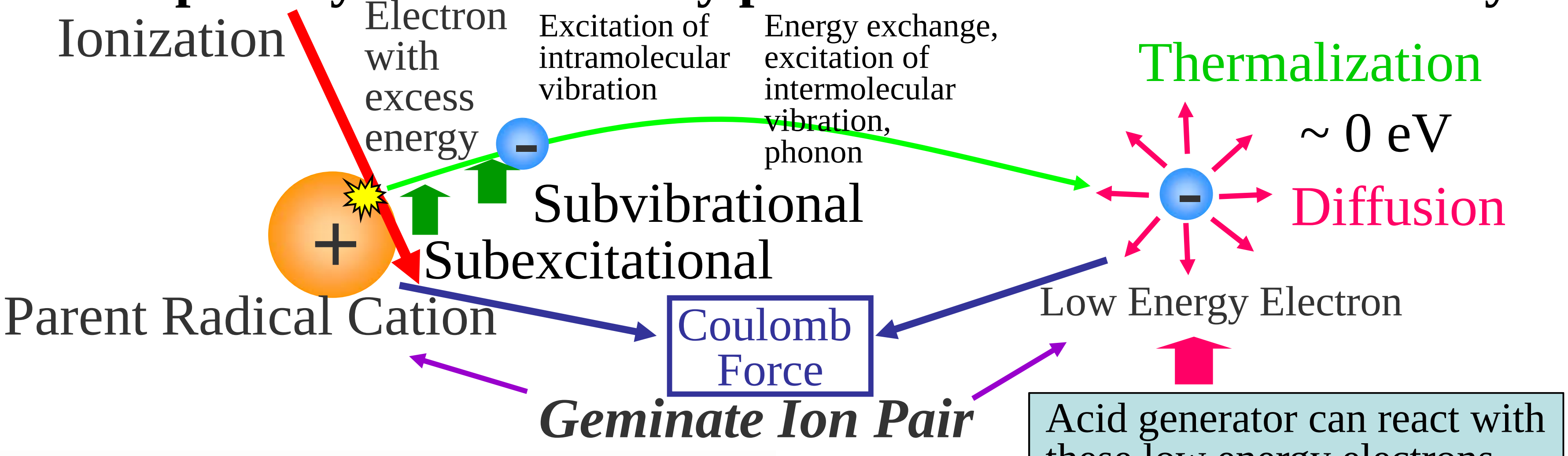
$H^+ + X^- \rightarrow HX$

If there is not geminate ion recombination process in nanospace acid generation, all most all acids are scavenged before chemically amplified reactions.

Most of acid generation is very fast and mainly produced in nanospace.



Nanospace dynamics in early processes of radiation chemistry



Ionization

Electron with excess energy

Excitation of intramolecular vibration

Energy exchange, excitation of intermolecular vibration, phonon

Thermalization

~ 0 eV

Diffusion

Subvibrational

Subexcitational

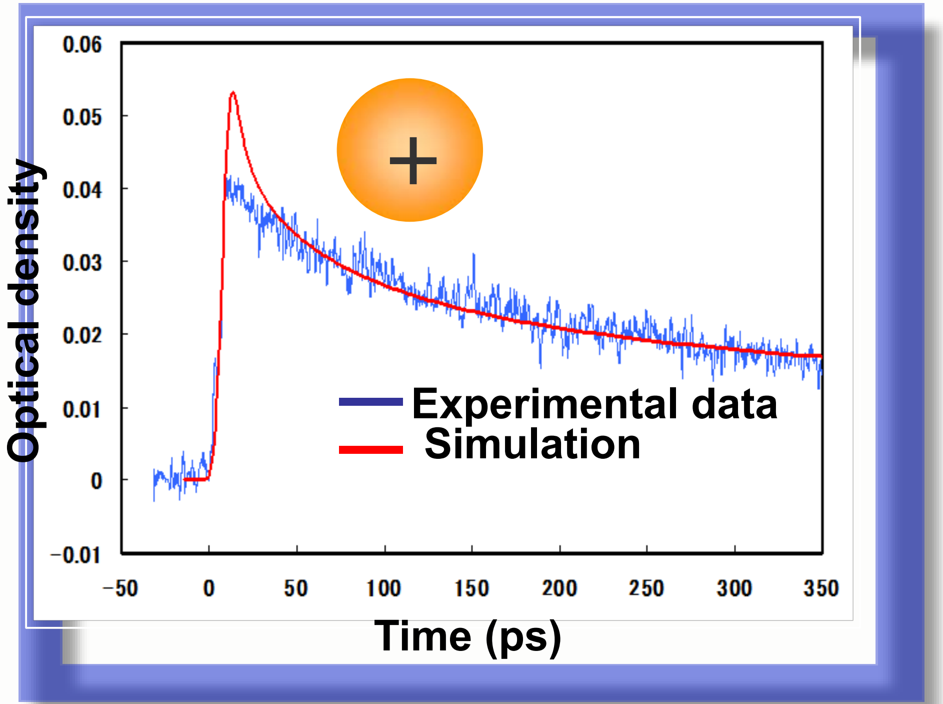
Parent Radical Cation

Coulomb Force

Low Energy Electron

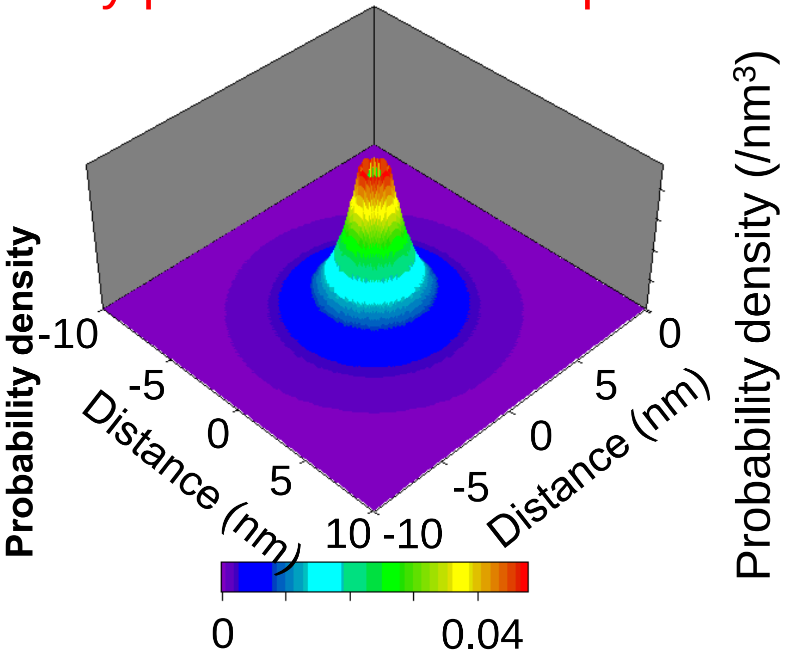
Geminate Ion Pair

Acid generator can react with these low energy electrons.



Experimental data of + obtained in the femtosecond pulse radiolysis and simulation

Acid generation is very fast and mainly produced in nanospace.



Nanospace (Geminate Ion Recombination) Reactions

Two reactions are important in nanospace reactions of EUV and EB CARs: Geminate ion recombination and dissociative electron attachment. We have studied these two processes more than 30 years by pulse radiolysis.

(geminate ion recombination: S. Tagawa, M. Washio, H. Kobayashi, Y. Katsumura, Y. Tabata, Radiation Phys. Chem.21, 45(1983) and S.Tagawa et al. , Radiation Phys. Chem.34,503(1989)
(dissociative electron attachment: S.Arai, S.Tagawa, M.Imamura, J. Phys. Chem. 78,519 (1974）

Pulse radiolysis of CMS (EB resist)

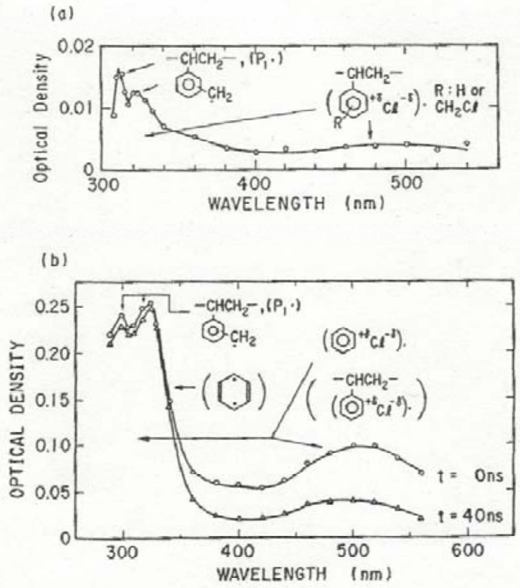
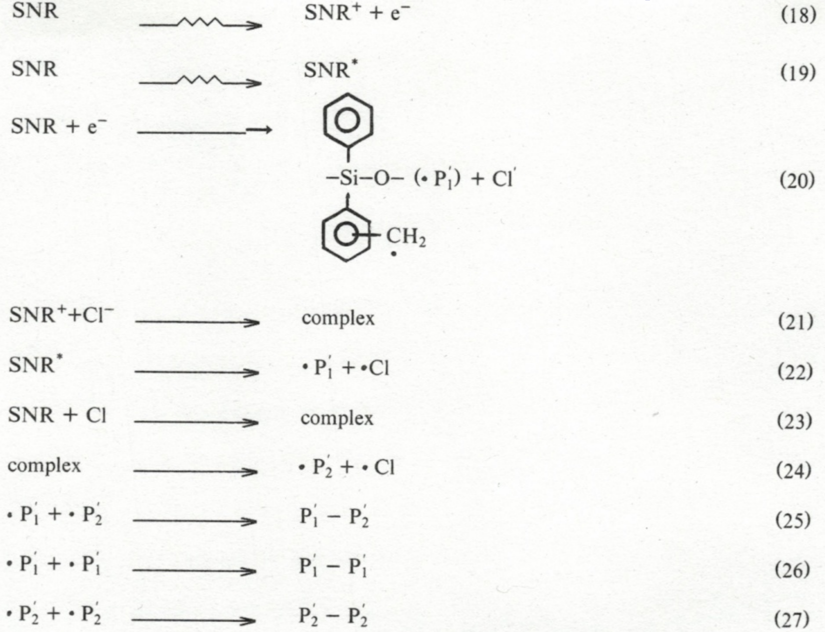


Figure 2. Transient absorption spectra observed in the pulse radiolysis of (a) CMS (chloromethylated polystyrene) solid film and (b) 200 mM CMS solutions in benzene immediately (o) and at 40 ns (Δ) after 2 ns pulses.

Reaction mechanism of SNR (EB resist)



$$\mathrm{SNR} \rightsquigarrow \mathrm{SNR^+ + e^-} \quad (18)$$

$$\mathrm{SNR} \rightsquigarrow \mathrm{SNR^*} \quad (19)$$

$$\mathrm{SNR + e^-} \longrightarrow \mathrm{-Si{-}O{-}\ (\cdot P_1') + Cl'} \quad (20)$$

$$\mathrm{SNR^+{+}Cl^-} \longrightarrow \mathrm{complex} \quad (21)$$

$$\mathrm{SNR^*} \longrightarrow \mathrm{\cdot P_1' + \cdot Cl} \quad (22)$$

$$\mathrm{SNR + Cl} \longrightarrow \mathrm{complex} \quad (23)$$

$$\mathrm{complex} \longrightarrow \mathrm{\cdot P_2' + \cdot Cl} \quad (24)$$

$$\mathrm{\cdot P_1' + \cdot P_2'} \longrightarrow \mathrm{P_1' - P_2'} \quad (25)$$

$$\mathrm{\cdot P_1' + \cdot P_1'} \longrightarrow \mathrm{P_1' - P_1'} \quad (26)$$

$$\mathrm{\cdot P_2' + \cdot P_2'} \longrightarrow \mathrm{P_2' - P_2'} \quad (27)$$

Acids and radicals are generated very efficiently by both geminate recombination and dissociative electron attachment in halogenated EB resists.(Y. Tabata, S.Tagawa, M.Washio, ACS Symposium Series 255, 151-163 (1984), S.Tagawa, Radiation Phys. Chem. 27, 455-459 (1986), S. Tagawa, ACS Symposium Series 346, 37-45(1987))

Quencher (Q) Effects on Acid Generation of EB & EUV CARs

Competition reactions

$H^{+} + Q \longrightarrow QH^{+}$

$H^{+} + X^{-} \longrightarrow HX$

The reaction of proton with Q and X^{-}

$$\frac{\partial w}{\partial t} = -kCw$$

Spur (Nanospace) reaction: $C_{X^{-}} < C_{Q}$

Bulk reaction: $C_{X^{-}} <<<<< C_{Q}$

Proton reaction rate (*k*) with of Q and X^{-}

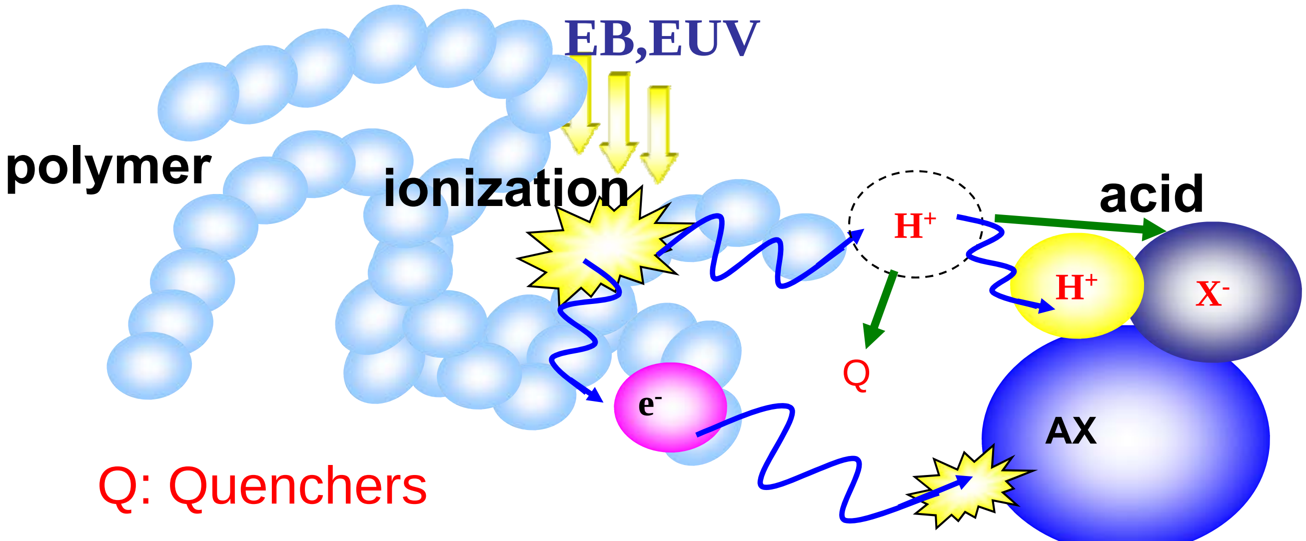
$$k = 4\pi RD$$

$R_{X^{-}}$ (Onsager Length) >> R_{Q} (molecular size)

D: H^{+} is mobile, Q , X^{-} are not mobile

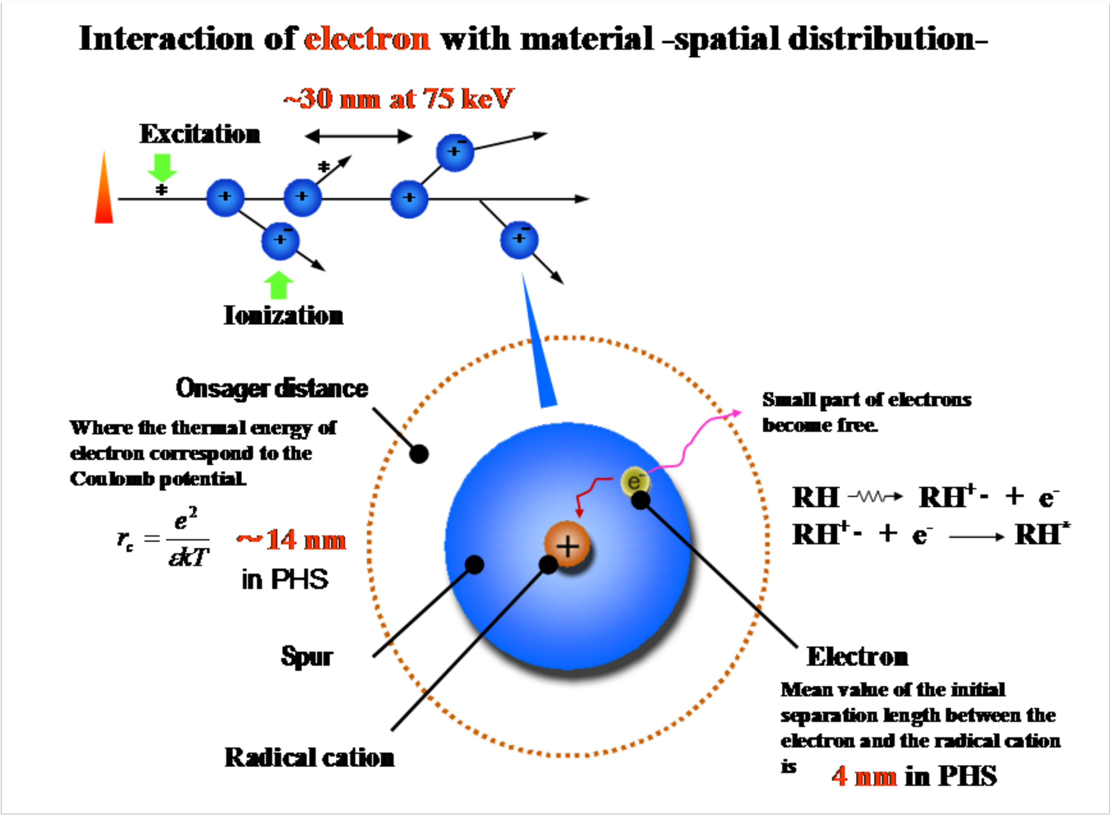
R: reactin radius, D: sum of diffusin constants

Almost all protons are scavenged in bulk before acid generation. Acid generation and scavenging reaction compete only in spur (nanospace).



Q: Quenchers

Investigation on nanoscale topography in resist



Interaction of electron with material -spatial distribution-

Onsager distance: Where the thermal energy of electron correspond to the Coulomb potential.

$$r_c = \frac{e^2}{\varepsilon k T}$$ ~14 nm in PHS

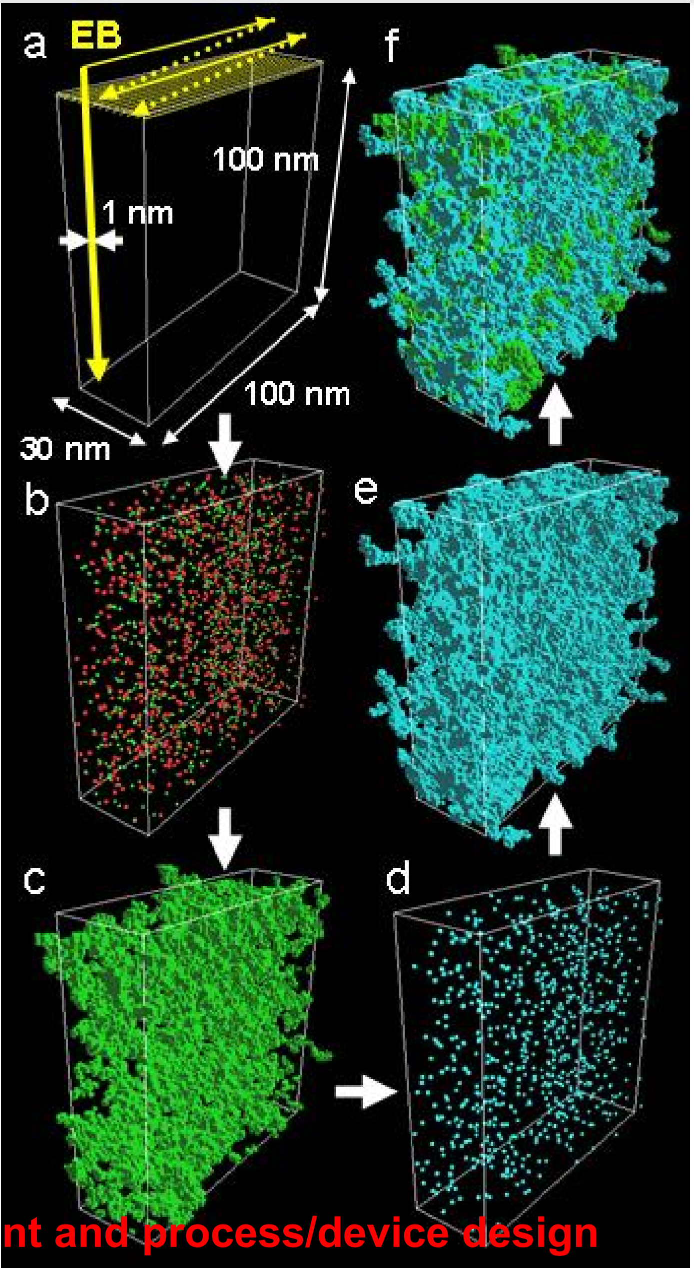
Small part of electrons become free.

$RH \rightsquigarrow RH^{+}\cdot + e^-$

$RH^{+}\cdot + e^- \longrightarrow RH^*$

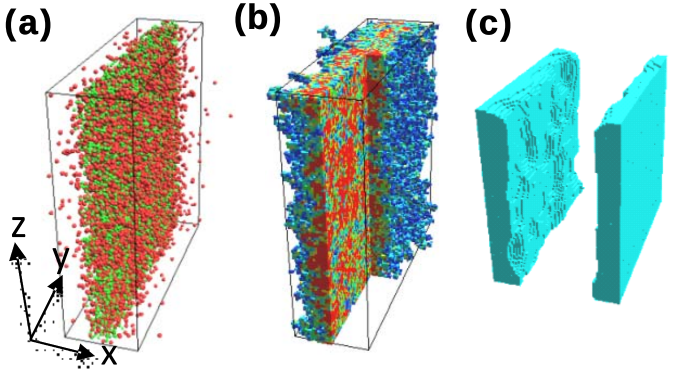
Electron: Mean value of the initial separation length between the electron and the radical cation is 4 nm in PHS

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

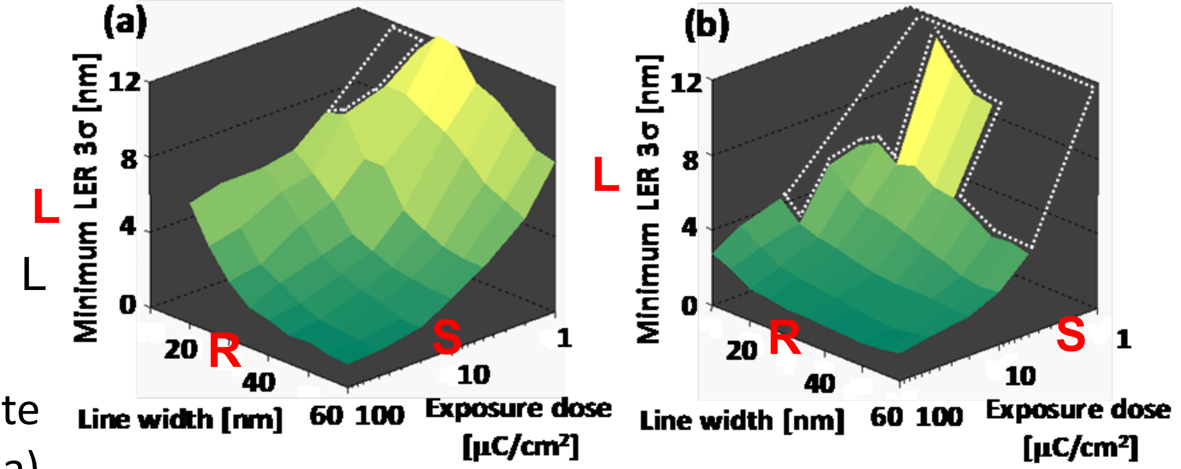


Establishment of basic science for material development and process/device design

RLS Trade-off Relation Simulated by Monte Carlo and Dissolution Simulations



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 exposed line width of 10 nm. The exposure dose and development time were 50 mC/cm^2 and 60 s, respectively. The axes x, y, and z in the left side of (a) represent the directions of exposed line width, line length, and film thickness, respectively. The black wire box is a 30 × 100 × 100 nm^3 cuboid.

The area enclosed by white dotted lines represents the failure in development.

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. [A. Saeki, T. Kozawa, and S. Tagawa, *Appl. Phys. Express* **2** (2009) 075006.]

Pattern Formation Mechanisms of EUV Resists

Comparison of Energy Absorption and Reaction Mechanisms among KrF, ArF, EB and EUV CARs

Energy Absorption Mechanisms

Resist	Energy absorption process	Main energy absorber
KrF,ArF	**Lambert's law**	Acid generator
EB	**Bethe equation** Energy absorption is proportional to electron density	Mainly Polymer
EUV	**Lambert's law** $\frac{dI(z)}{dz} = -\alpha I(z)$	Mainly Polymer

Reaction Mechanisms

Resist	Main Initial reactions of acid generation
KrF,ArF	Excitation of acid generators
EB	Mainly **isolated spur** reaction 1. Ionization of polymers 2. Dissociative electron attachment of acid generators 3. Geminate recombination of protons and anions
EUV	Mainly **multi-spur** reactions 1. Ionization of polymers 2. Dissociative electron attachment of acid generators 3. Geminate recombination of protons and anions

S. Tagawa, MNC2007 Plenary Lecture

Interaction of EUV photon with CARs

-spatial distribution-

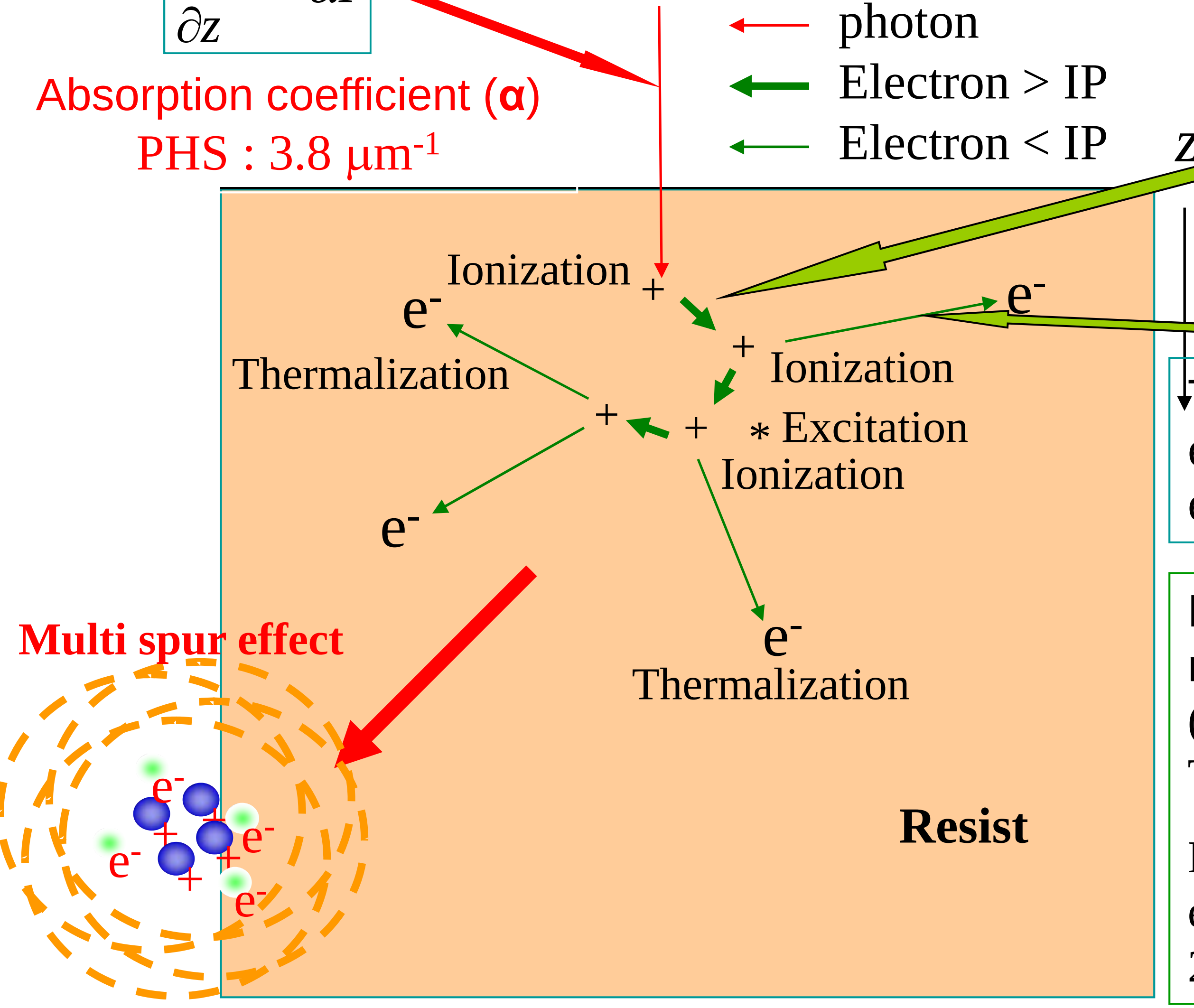
Lambert's law

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** nm for PHS

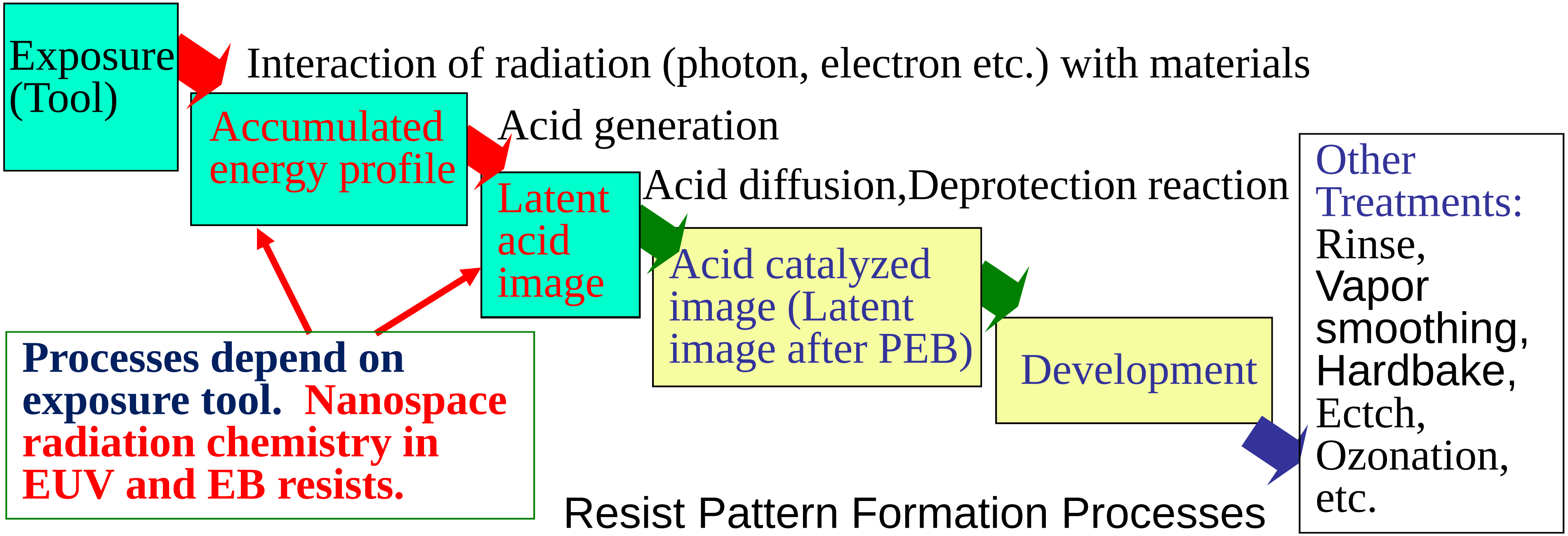
The number of secondary electrons is estimated expermentally. **4.2** for PHS

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)

Conclusion

1. The relation between RLS trade-off and radiation chemistry was made clear.
2. The importance of nanospace radiation chemistry in resist pattern formation in EUV and EB resists was also made clear.



Exposure (Tool)

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

Accumulated energy profile

Acid generation

Latent acid image

Acid diffusion,Deprotection reaction

Acid catalyzed image (Latent image after PEB)

Development

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

Processes depend on exposure tool. Nanospace radiation chemistry in EUV and EB resists.

Resist Pattern Formation Processes

The improvement at each stage is required cloth to its physical and chemical limit. The good integration of improvement at each stage with mutual stage interactions is strongly needed for steady progress in the development of next generation EUV and EB resists.

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