

Trade-off Problems among Resolution, LWR and Sensitivity of EUV Resists

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Approaches to address the EUV resist challenges of image collapse, LWR, sensitivity, and resolution

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Osaka University

- (**New Laboratory**) Beam Application Frontier Laboratory (**Director**) Drs. **H.Yamamoto, K. Enomoto, Prof. Endo et al.**
- Nanofabrication Function (**Head**), Handai Multi-Functional Nanofoundry Nonotechnology **Dr. A. Oshima** et al.
- Research Laboratory for Quantum Beam Science :**Pulse Radiolysis Facility**

Selete (Semiconductor Leading Edge Technologies)

Researchers in Industrial Companies and Universities

Waseda University (Guest Professor) Prof. M. Washio, Graduate Students (T. Gowa.)

EUV resist net of URVIC (University, Research Institute, Venture Company, Industry, Consortia) net (**Chairman**)

Old coworkers: Prof. Tabata, past students (Prof. M. Washio & Y. Yoshida), NTT resist researchers

Critical Issues and Requirements of EUV Resist Development

- **Past and Now:**
RLS (Resolution, LWR and Sensitivity) trade-off problem.
Increase in pattern formation efficiency
Image collapse
Outgas
- **Near Future:**
The reduction of LWR
Increase in chemical gradient and decrease in chemical inhomogeneity at image boundary
- **Future:** The more detailed research on **nanospace reactions** and **molecular interactions** in EUV and EB resists
- **Always:** Industries want the help of radiation chemists for not only solutions of high sensitive resists but also many problems such as radiation damages and radiation-induced contamination.

What is RLS Trade-off Problem

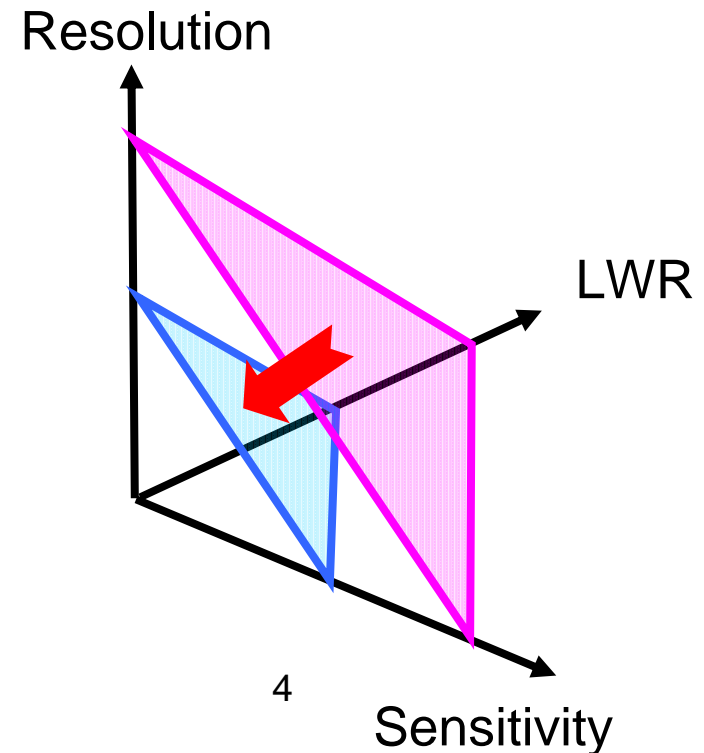
The Most Critical Problem of EUV Resist Development Today

5mJ/cm² EUV resists were required for early stage of EUV lithography development. Chemically amplified resists were considered to be candidates, but the resolution limit of chemically amplified resists were considered to be 50/60 nm at that time.

After the development of the EUV chemically amplified resists with sub-50 nm resolution started, many researchers had arrived at the RLS (Resolution, LWR, Sensitivity) trade-off triangle around 2003.

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

It was very difficult to improve resolution, LWR, and sensitivity, simultaneously. Resist development almost stopped several years at that time.

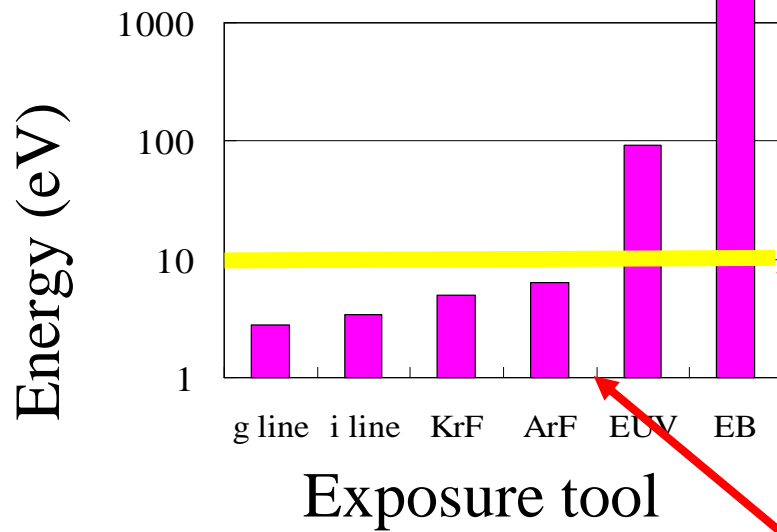


What is the Origin of RLS Trade-off Problem

- It occurred in chemically amplified resists (CARs) with high concentration of quenchers for sub-50 nm resolution.
- 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 required less than 40 nm resolution. So RLS trade-off appeared in EUV resist research at first.

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.

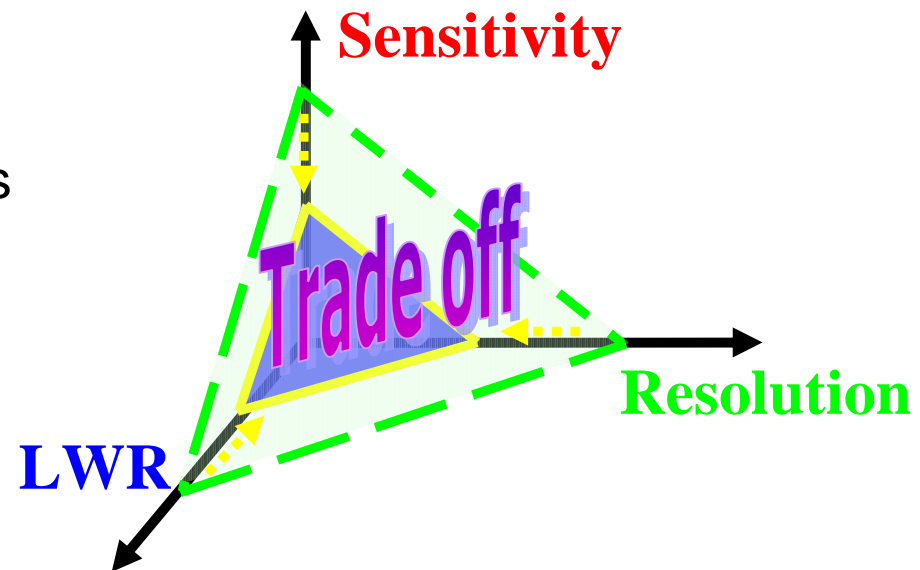
Ionization Potential of Resist Materials (~10eV)

RLS Trade-off Problem

Simulation (mathematics) by Gallatin in 2005 clearly explained RLS trade-off **without acid generation mechanisms**. In simulation, no fundamental differences exist among ArF, EB and EUV resists after acid generation.

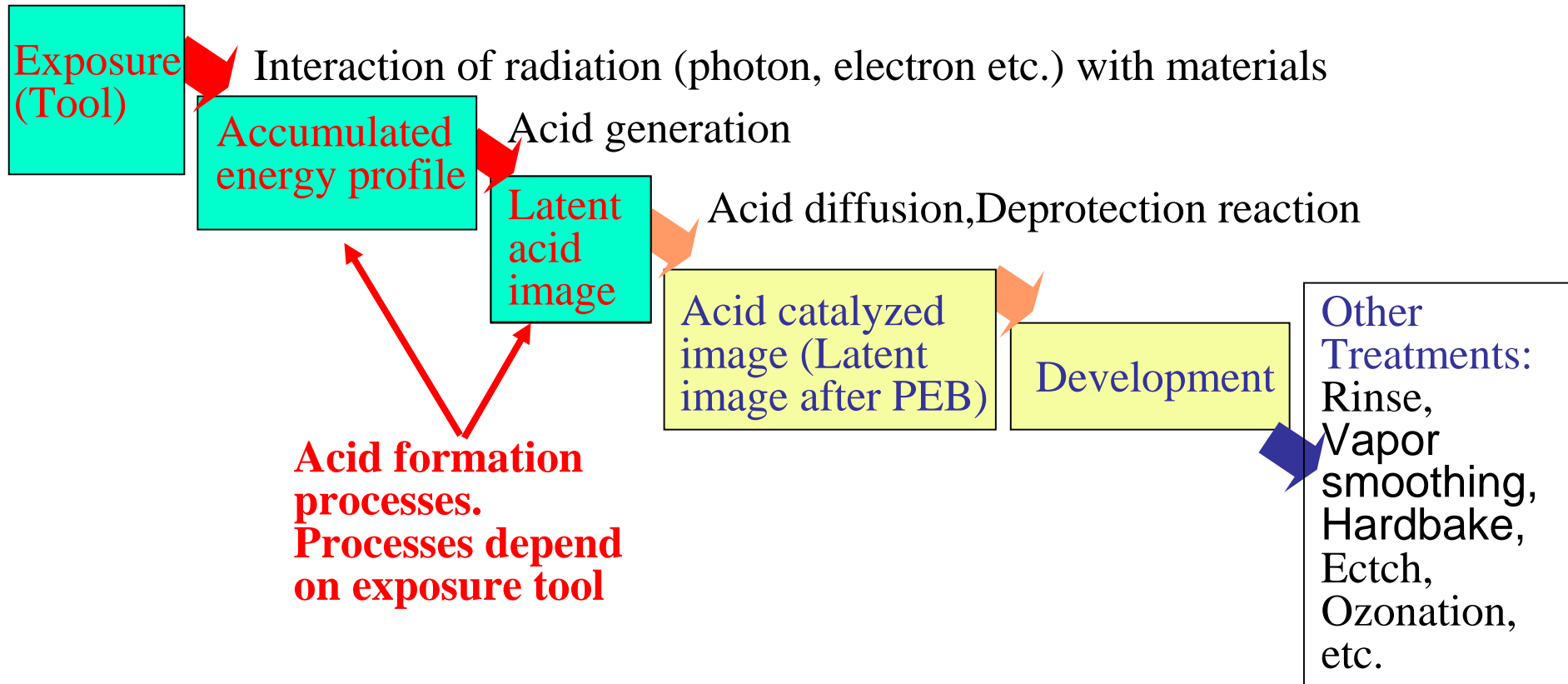
RLS trade-off is not specific.

Therefore, most of resist researchers except for us studied processes mainly after acid generation in early research stage of RLS Trade-off problem.



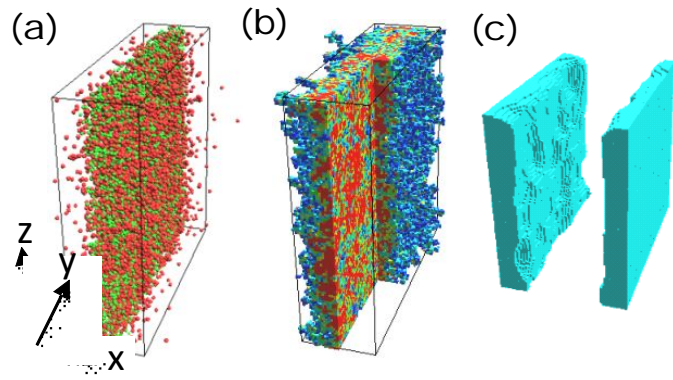
But we thought the acid generation mechanisms, especially **nano-space (geminate recombination)** reactions are important and essential for the solution of RLS trade-off problem, because the high acid yield and the small acid space distribution are clearly the best solutions of RLS trade-off problem.

Resist pattern formation processes



The high acid yield and the small acid space distribution are determined in acid formation processes.

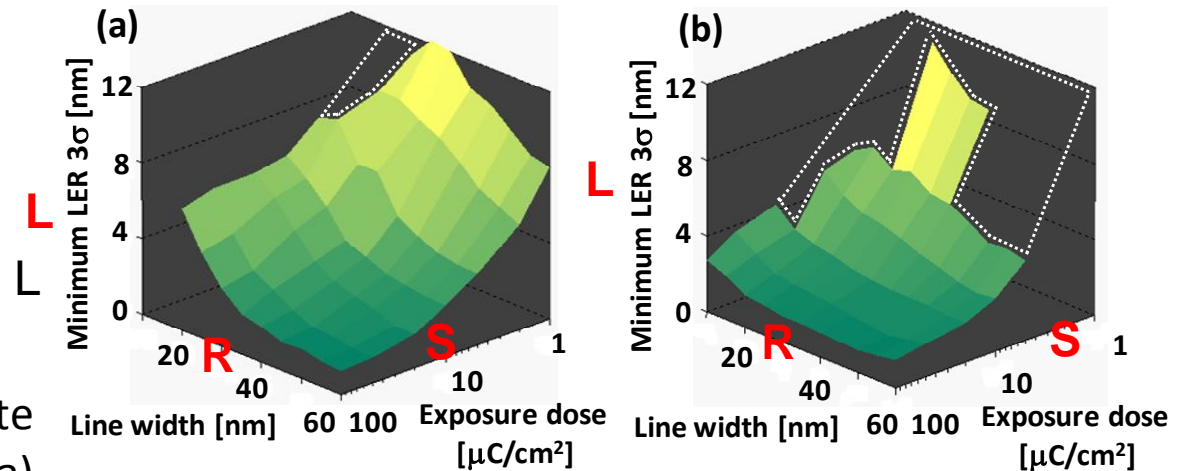
RLS Trade-off Relation Simulated by Monte Carlo and Dissolution Simulations



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.

The exposed line width of 10 nm. The exposure dose and development time were 50 mC/cm² 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 nm³ cuboid.

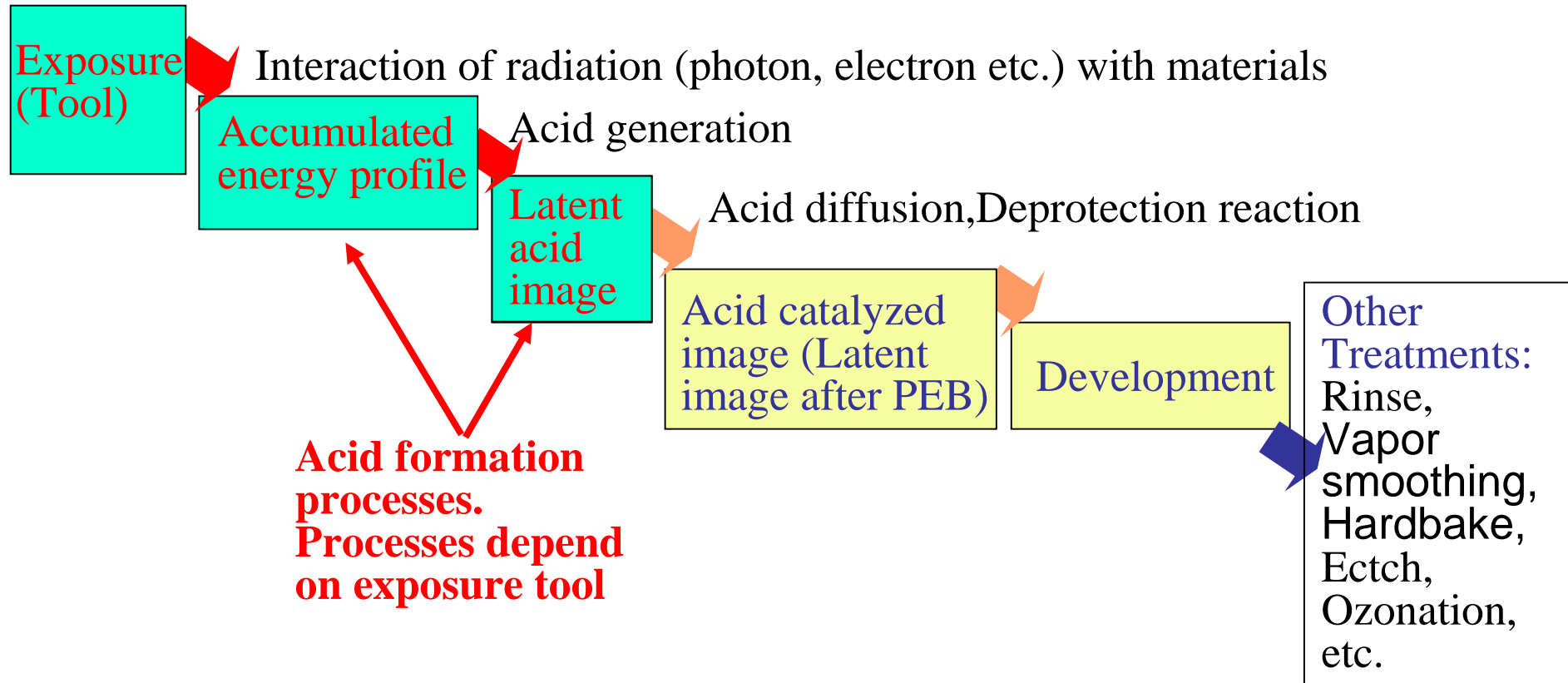
The area enclosed by white dotted lines represents the failure in development.



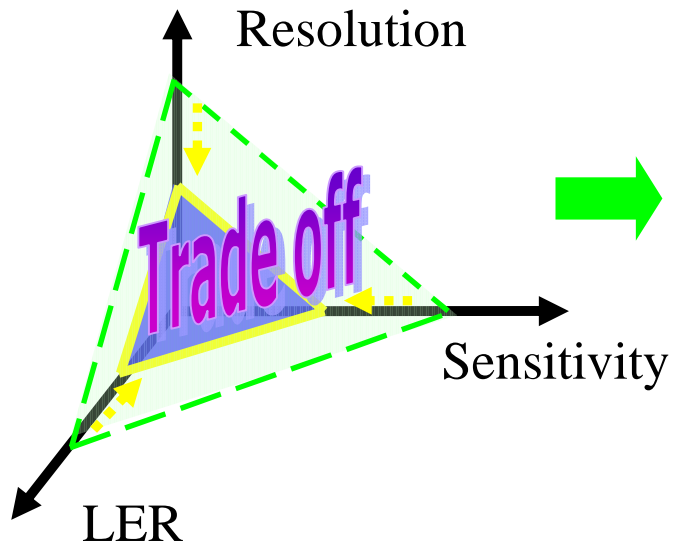
RLS relationship of developed line pattern at optimized PEB and development time. The exposed line widths of (a) and (b) are 30 and 10 nm, respectively.

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

Resist pattern formation processes



The high acid yield and the small acid space distribution are determined in acid formation processes.



The increase in pattern formation efficiency is required to simultaneously meet the requirements for solution of RLS trade-off problem.

Pattern formation efficiency before acid generation

||

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

Exposure
source
dependent

X

Limited by side wall degradation

Quantum yield of acid

Limited by secondary electron
emission efficiency

Interaction of EUV photon with CARs

Lambert's law

Intensity of EUV (I)

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

Absorption coefficient (α)

PHS : $3.8 \mu\text{m}^{-1}$

-spatial distribution-

EUV photon (92.5 eV)

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

Inelastic mean free path

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

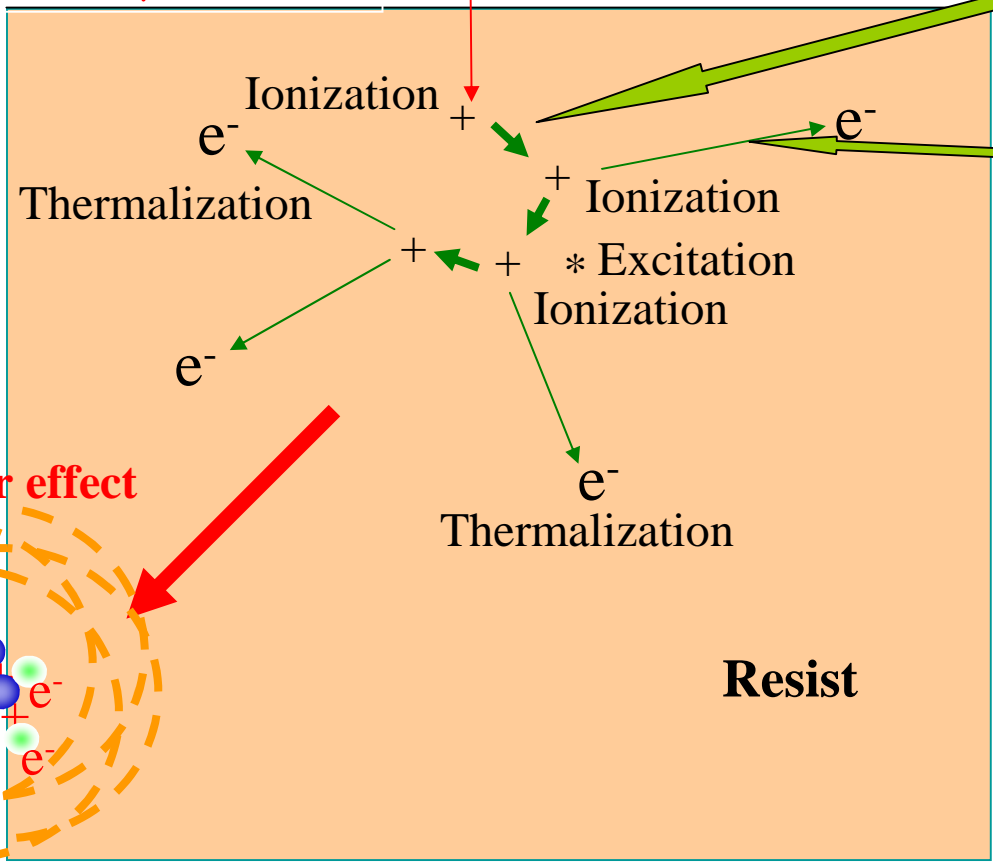
Thermalization Length
4.0 nm for PHS

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

PHS with 10 wt% TPS-tf

Acid molecules per photon: 2.6 (Kozawa et al. J.Vac.Sci. Technol.,B25(2007) 2481)

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



Multi spur effect

Resist

Results

Wt% of Fluorine atom per Fluorinated polymer	Absorption coefficient (μm^{-1})		Acid yield
	Caluculation value	Experimantal value	
63	9.9	7	1.6
51	8.9	8.6	1.7
38	7.8	8.1	1.9
25	6.6	6.6	2.3
0	3.8	4	2.4

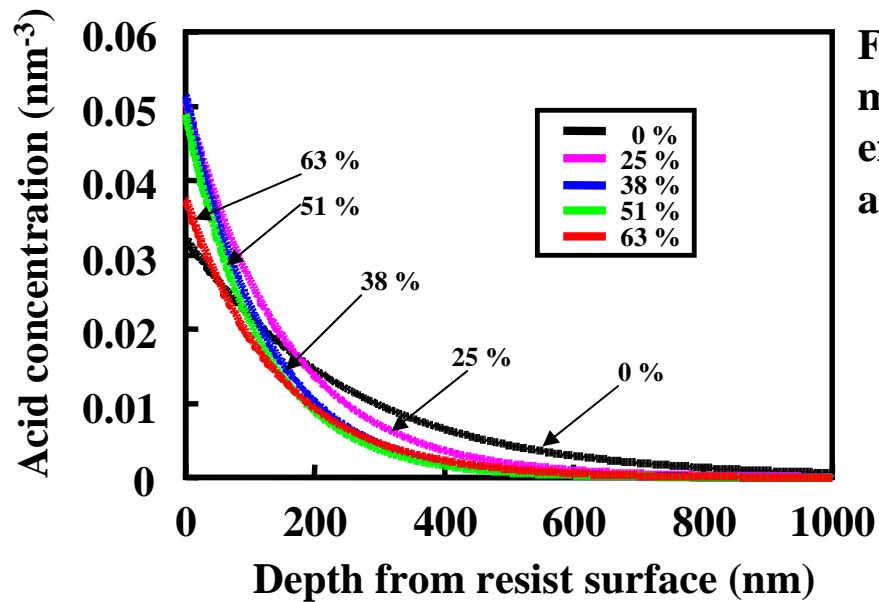
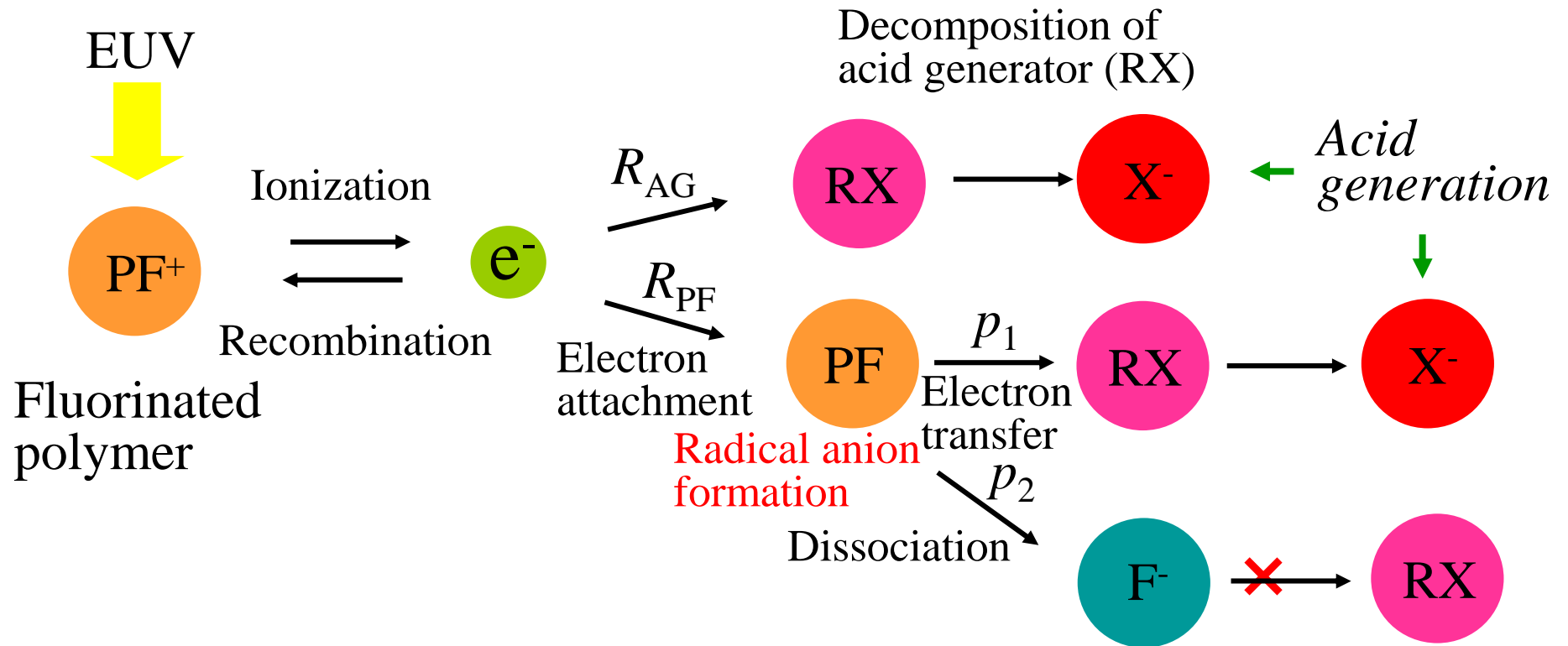


Fig. Depth profile of acid concentration (the number of molecules per unit volume) calculated on the basis of experimental data of acid generation efficiency and absorption coefficients at the exposure dose of $5 \text{ mJ}/\text{cm}^2$.

Theoretically the yield is 2.6 times based on photoabsorption process, but experimentally 1.5 times. The control of the reaction mechanism is not enough until at that time
Ultra thin film resists is important.

Clarification of Electron Flow in Chemically Amplified Resist



R : Effective reaction radius

p : Probability ($p_1 + p_2 = 1$)

depends on the lifetime of PF radical anion

Radiation Chemistry of Fluorinated Aromatic Compounds

8FN radical anion

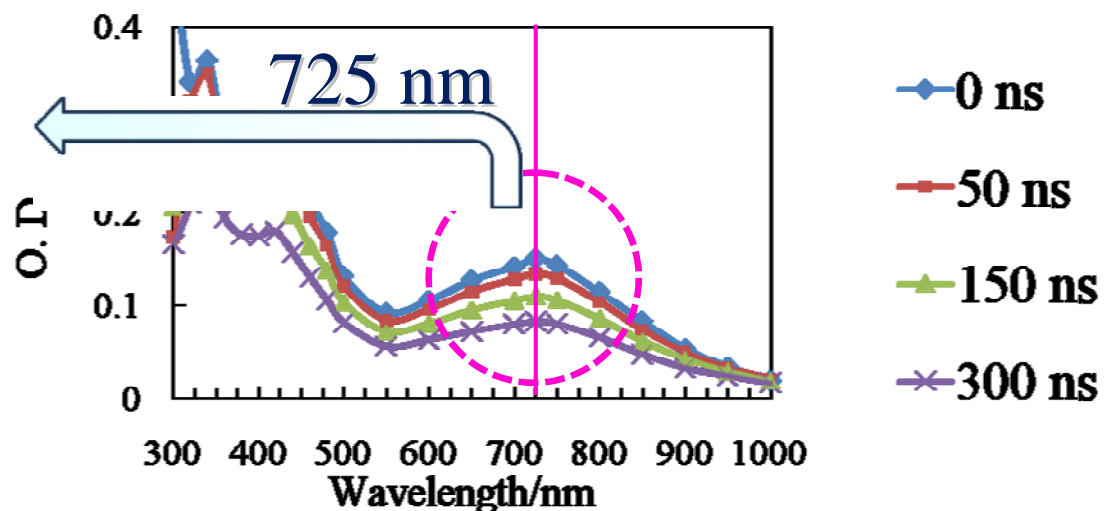
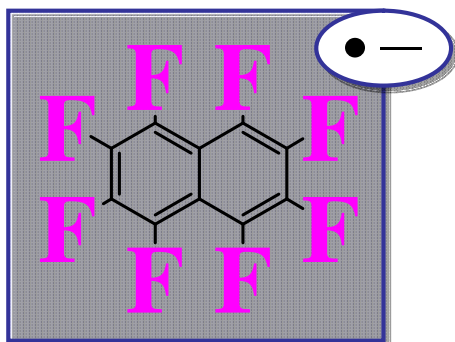


Fig. Transient absorption spectra of 100 mM 8FN solution in THF. (♦; immediately after the pulse(0 ns) ■; 50 ns ; 150 ns ×; 300 ns).

1FN radical anion

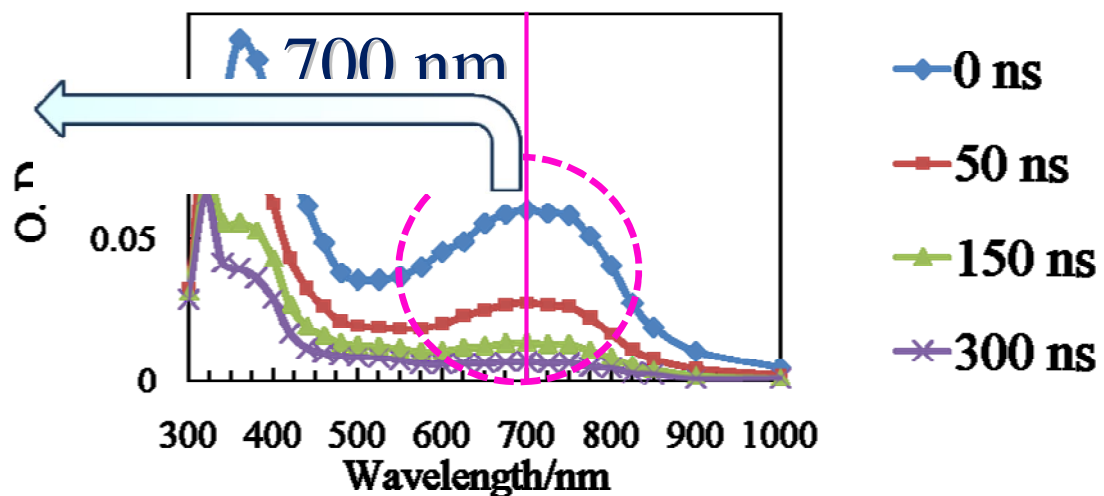
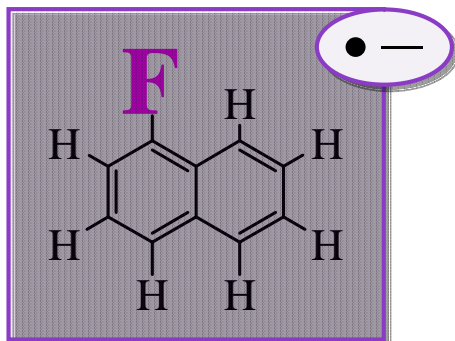
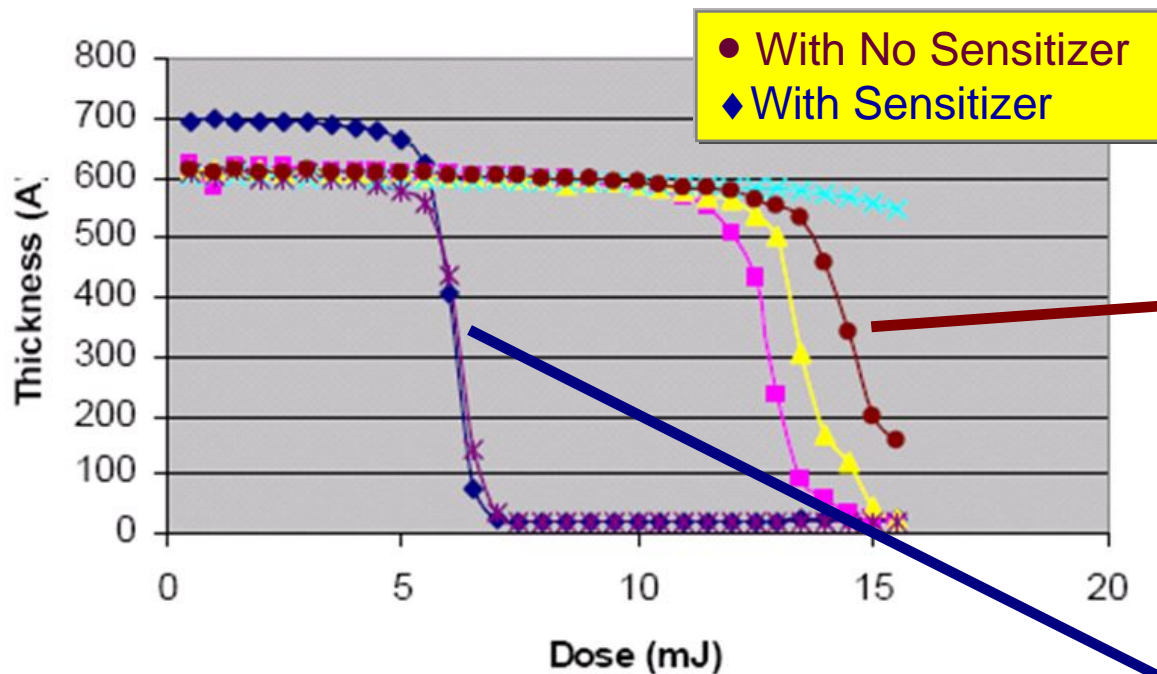


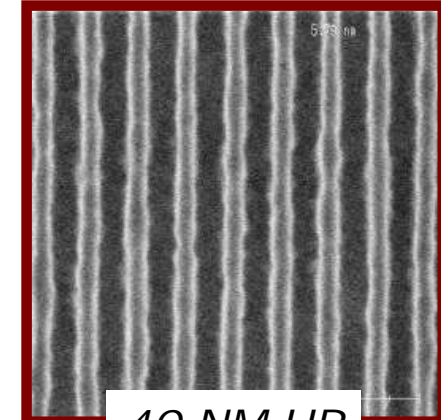
Fig. Transient absorption spectra of 100 mM 1FN solution in THF. (♦; immediately after the pulse(0 ns) ■; 50 ns ; 150 ns ×; 300 ns).

EUV Mechanism¹ Provides RLS Gain?

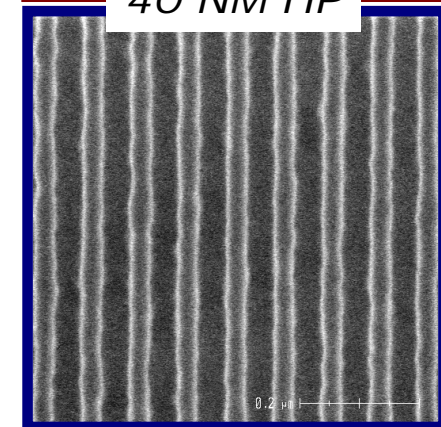
(from Todd R. Younkin, Intel, Litho Forum 2008)



Resist A
S=13.8 mJ; L<5.5 nm



40 NM HP



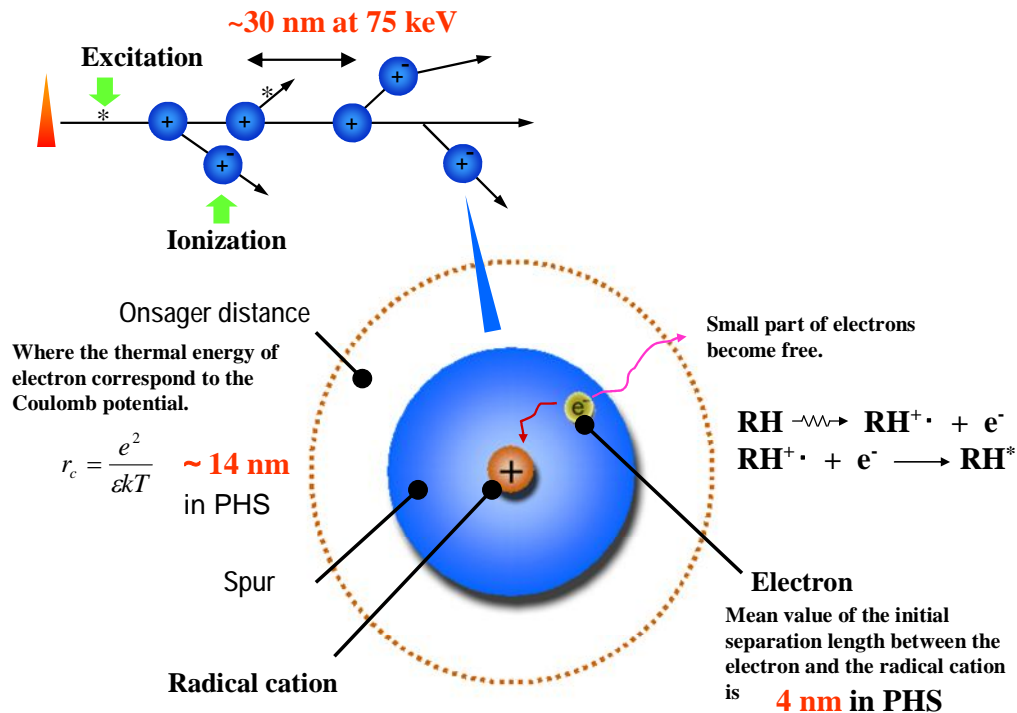
Resist B
S=7.0 mJ; L<5.0 nm

- 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

¹Kozawa, et al. JVSTB 25, 2481 (2007)

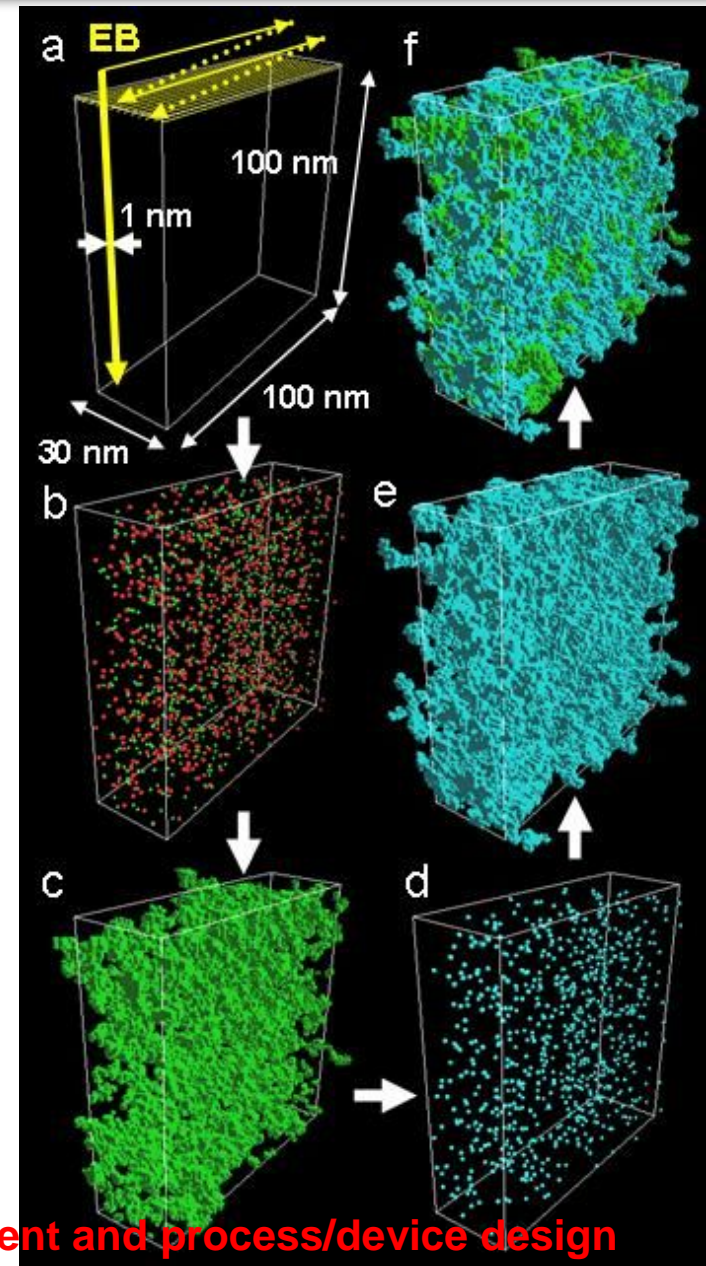
Investigation on nanoscale topography in resist

Interaction of **electron** with material -spatial distribution-

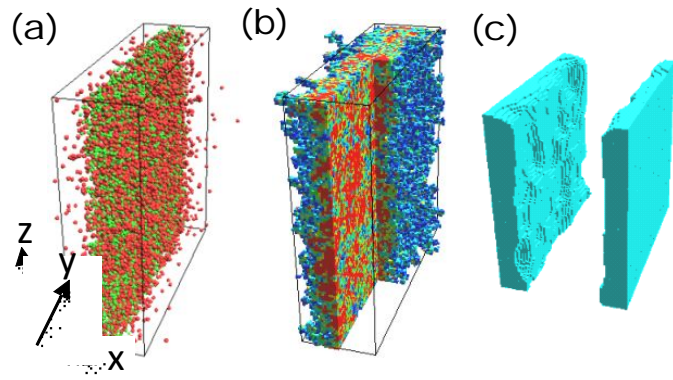


We elucidated the formation mechanism of resist pattern from the viewpoints of the interaction of EB reaction with films based on huge amount of experimental results such as pulse radiolysis, subsequent radiation chemical reactions, and diffusive reactions

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



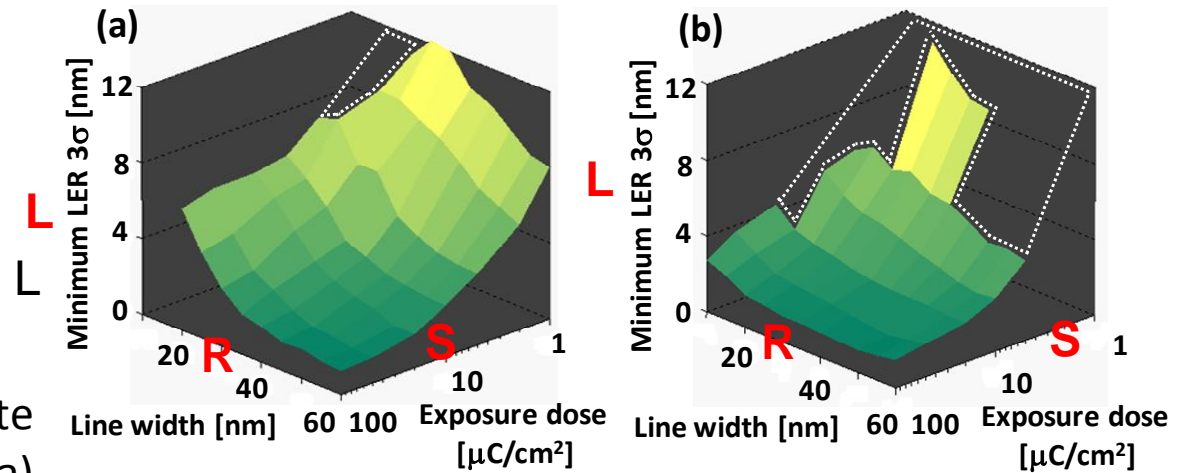
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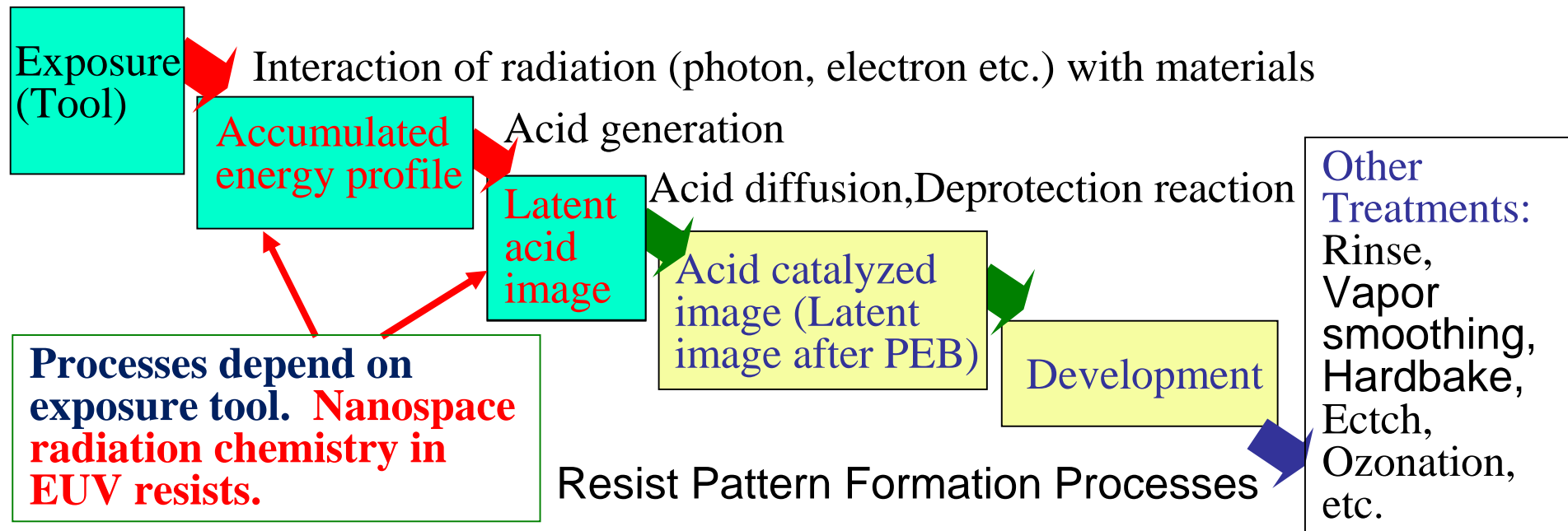
Many kinds of methods to improve RLS trade-off and LWR.

- High Absorption
- High Yields of Acids
- Diffusion Control Reactions
- Improvement of Development
- Polymer-bound PAG Resist System
- Variable Acid Diffusion Type Resists
- Treatments after Development
- Molecular Resists
- Many Other Methods

Conclusion

Today critical Issues and requirements of EUV resist development past and now, that is, how to solve RLS trade-off and how to increase in pattern formation efficiency are summarized.

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



The improvement at each stage is required cloth to its physical and chemical limit.

Anisotropic acid diffusion

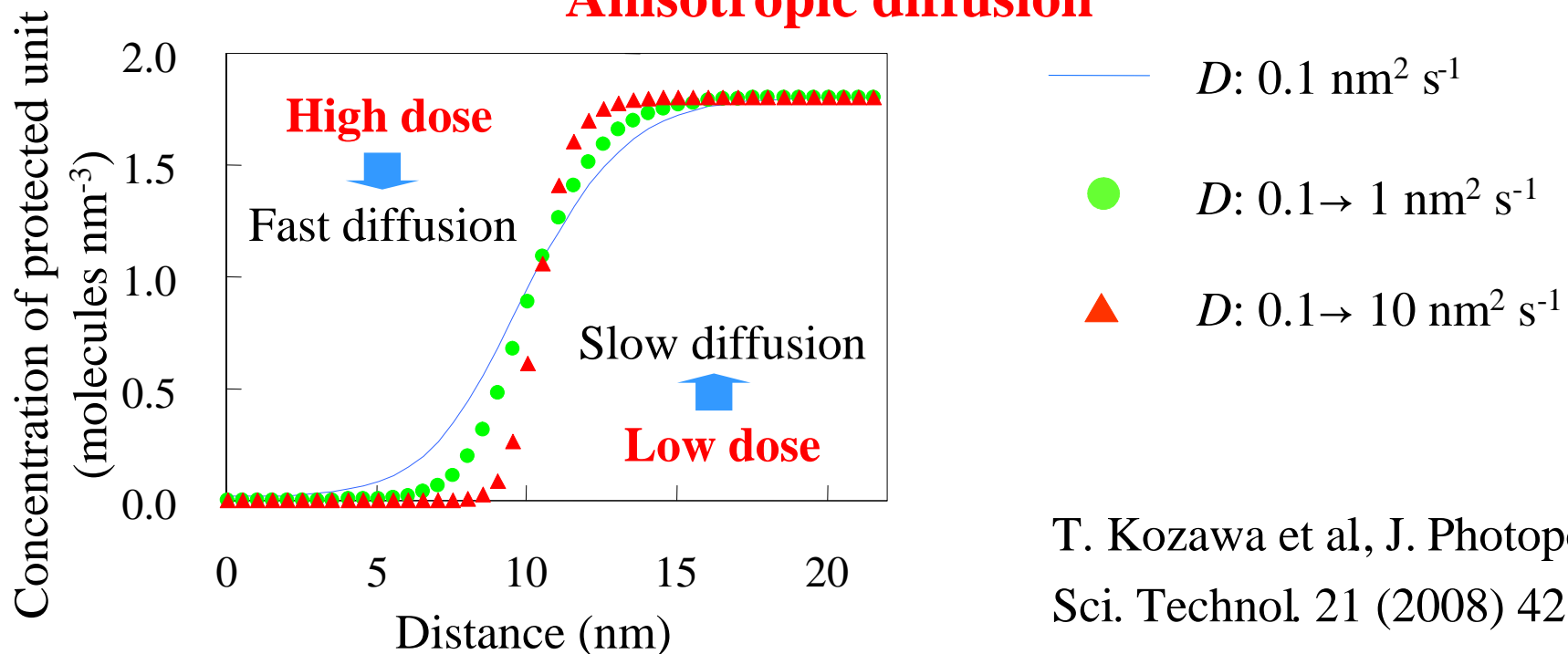
Diffusion coefficient depends on matrix.

In high dose region, the environment surrounding acid molecules significantly changes during the catalytic chain reactions.

Nonpolar to polar
Generation of byproducts
(low molecular contents)
Increase in free volume etc.



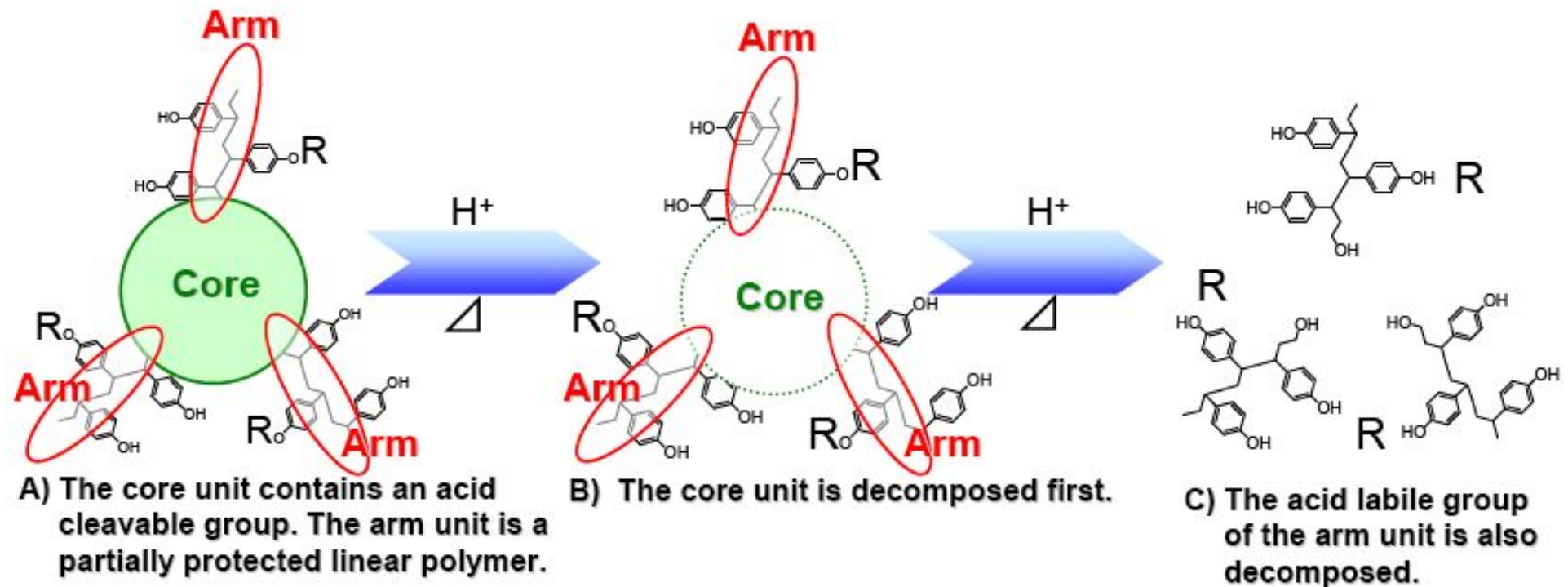
Anisotropic diffusion



T. Kozawa et al, J. Photopolym Sci. Technol. 21 (2008) 421.

What is STAR polymer ?

J. Iwashita et al., Proc. SPIE 7273 (2009) 727330.



Chemical concept for STAR shaped polymer

Lithographic performance comparison (Resolution)

Resolution comparison of Linear and STAR polymer

	30nmHP	28nmHP	26nmHP	24nmHP	22nmHP
Linear25-M Esize ~ 18.4mJ LWR=4.4nm UR ~ 30nm HP DOF ~ 120nm					
STAR25-M Esize ~ 16.8mJ LWR=4.1nm UR ~ 28nm HP DOF ~ 230nm					

Lithographic Condition

- Exp. Tool : Micro Exposure Tool
- Substrate : B-ARC
- Resist thickness : 60nm
- PAB : 80°C-60s
- Illumination : NA 0.3, Annular
- PEB : 80°C-60s
- Development : TMAH 2.38%aq , 60s

J. Iwashita et al., Proc. SPIE 7273 (2009) 727330.

SPIE Advanced Lithography Feb. 24, 2009

tak

Sensitivity and Shot Noise of CAR and non-CAR.

5 mJ/nm² is about 3 EUV photons/(1 nm)².

It is very difficult to overcome shot noise problem in non-CAR.

In CAR, the recombination reaction of acids and quenchers occurs in image boundary. LER is determined at image boundary. Acid diffusion decreases shot noise in CAR.

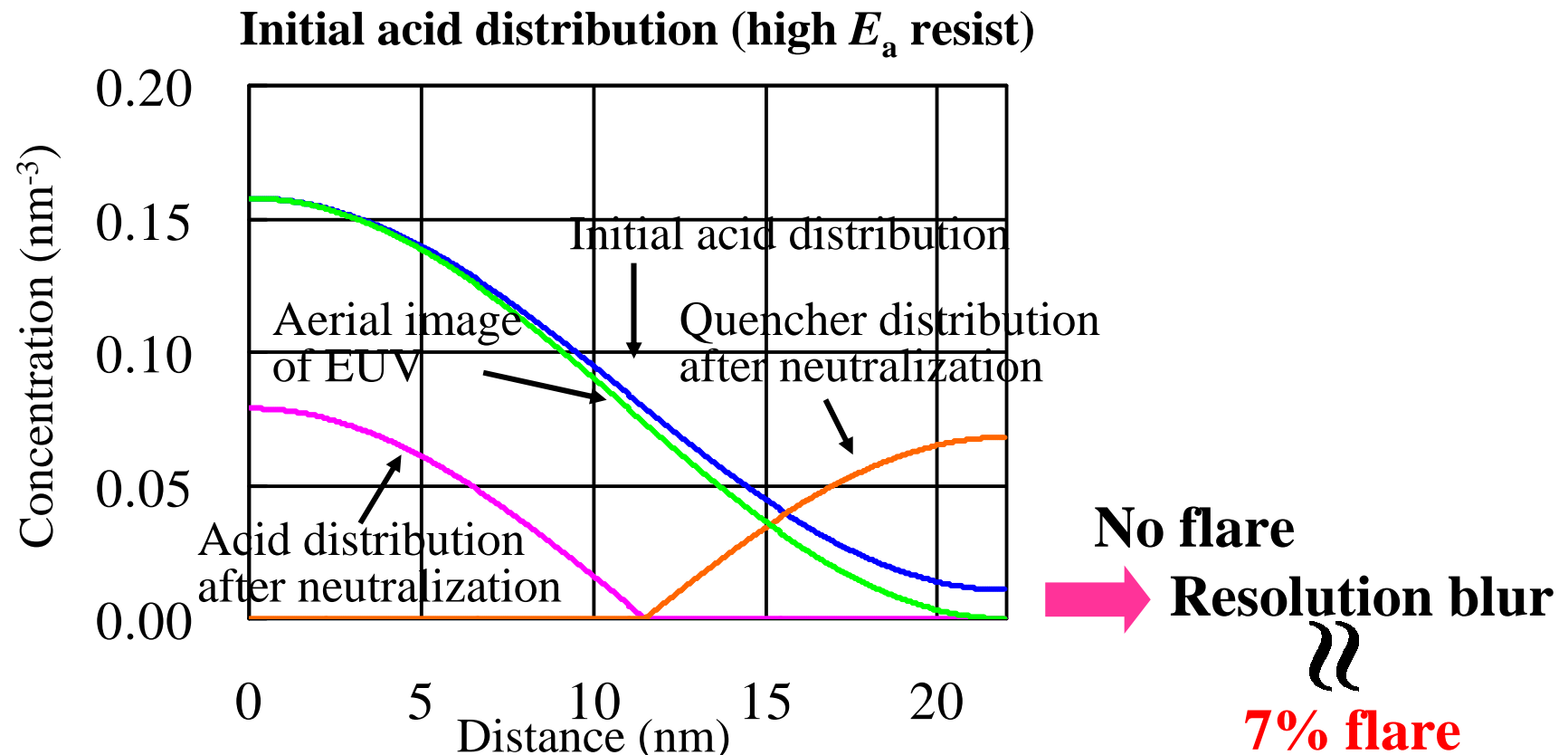


Fig. The aerial image of incident EUV (arb. unit) and the initial acid distribution (molecule nm⁻³).. (Jpn. J. Appl. Phys. 47 (2008) 4926).