Recent Progress in Nano-space Radiation Chemistry Research on Sensitivity Enhancements of EUV Resists

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Contents

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(2) Acid amplified resists (High Yield Acids)

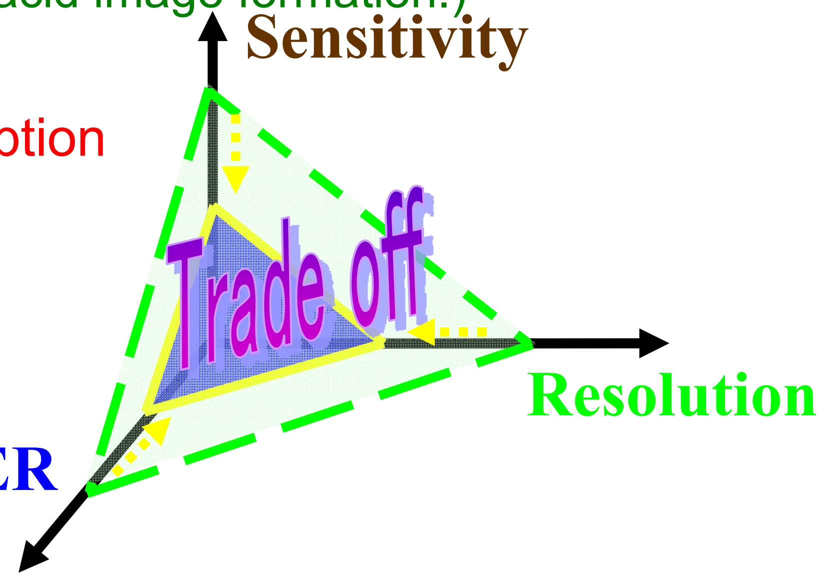
(3) EUV resists at 6.x nm (Future Problem)

RLS Trade-off Problem

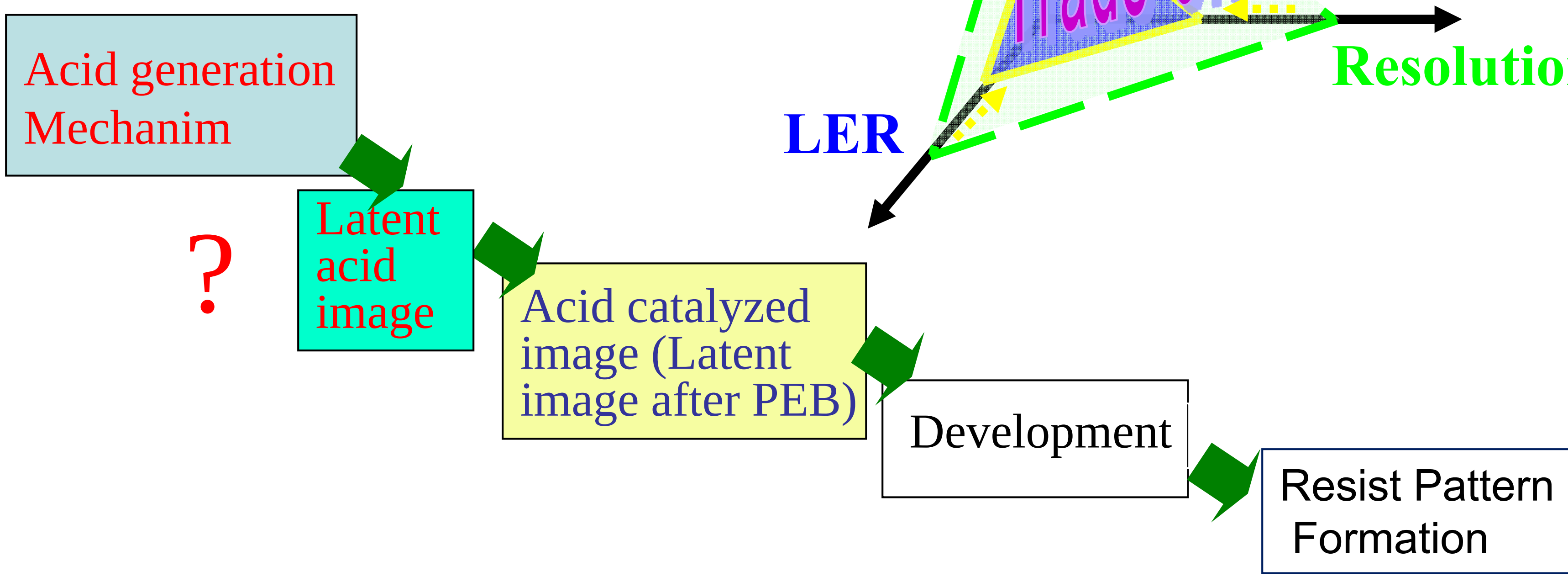
Most researchers had arrived at the RLS trade-off triangle.

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

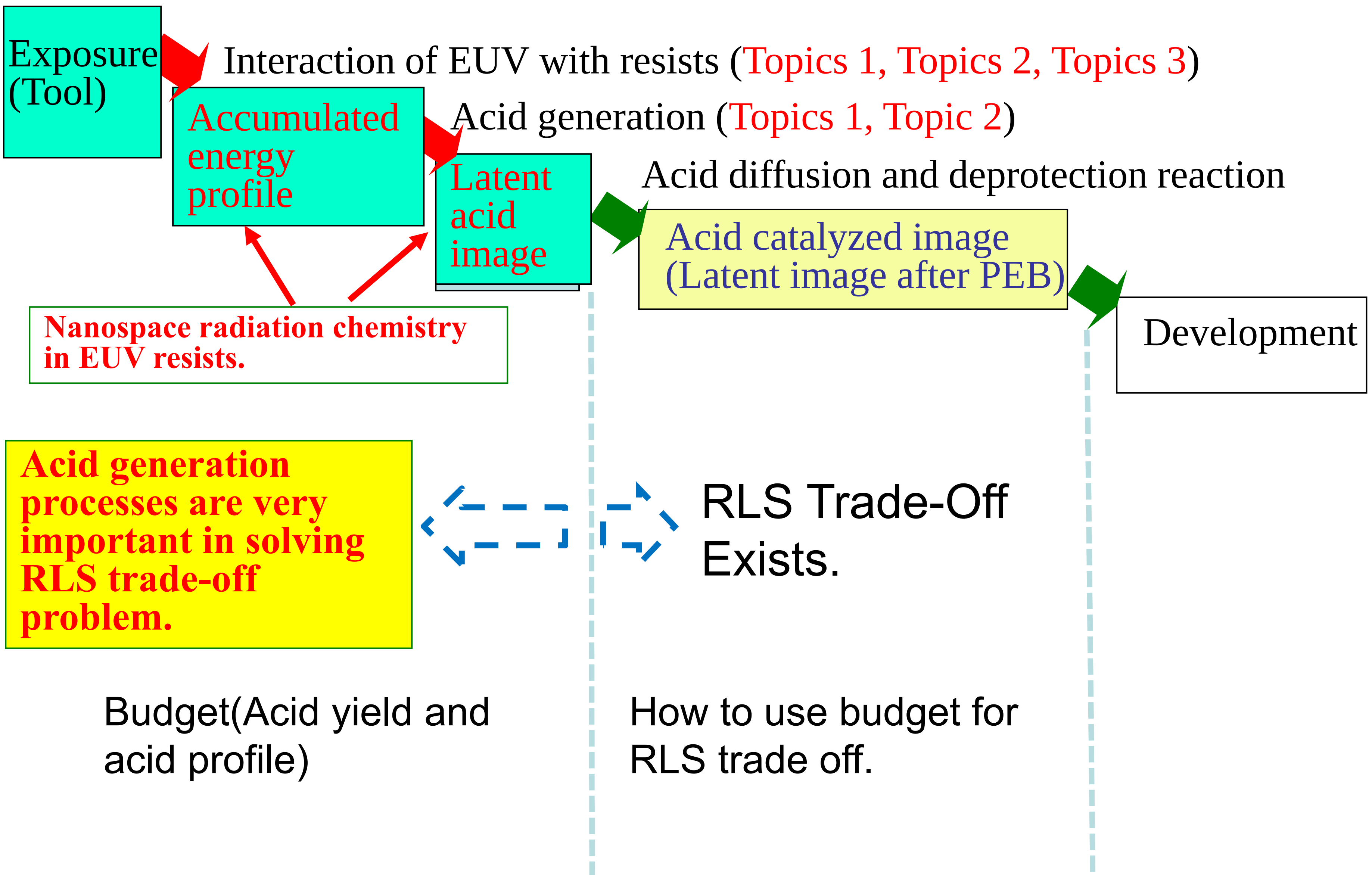
Simulations: *G.M. Gallatin, Proc. SPIE (2005)* (Simulations does not contain EUV - induced acid generation mechanism and no fundamental differences in simulations among ArF, EB and EUV resists after latent acid image formation.)



Latent Acid Image Distribution: Assumption

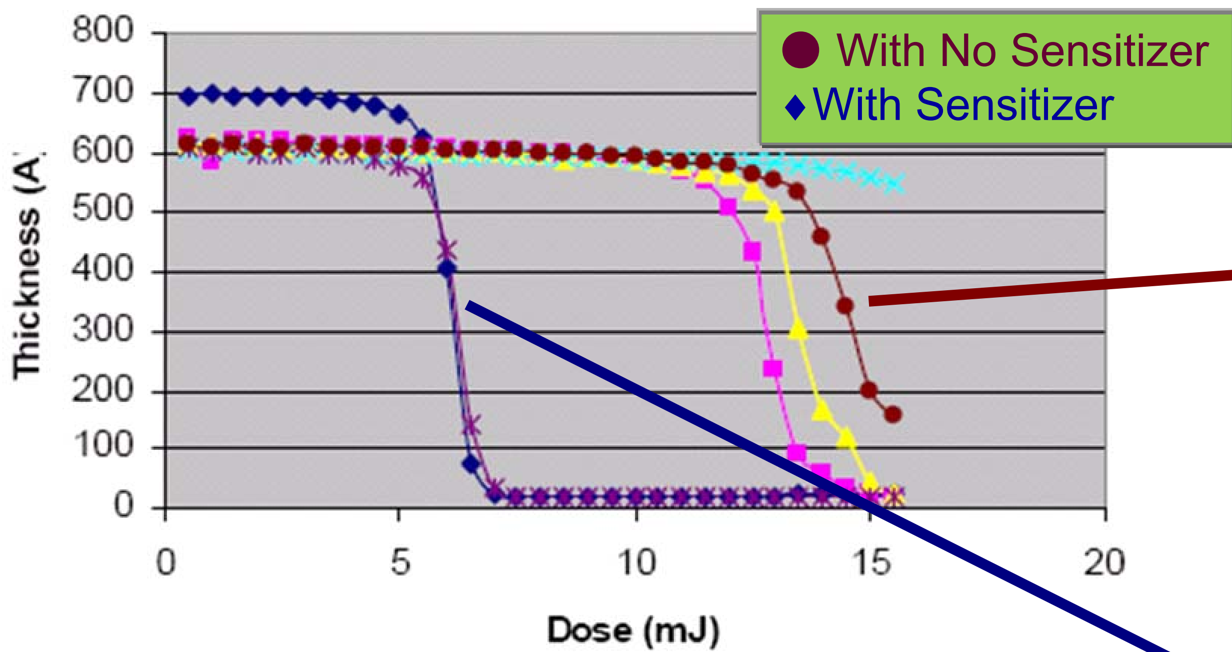


Resist Pattern Formation Processes of EUV Resists

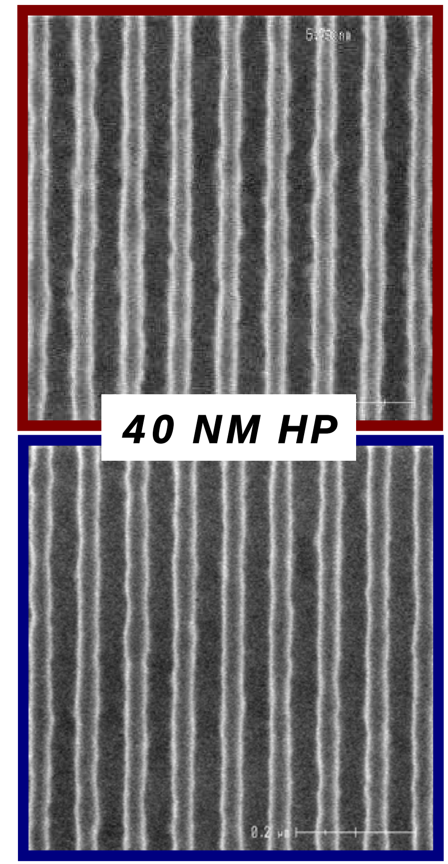


EUV Mechanism[1] Provides RLS Gain?

[1]Kozawa, et al. JVSTB 25, 2481 (2007)



Resist A
S=13.8 mJ; L<5.5 nm



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, No Degradation in LWR**

➩ **Multiple Suppliers Achieving Similar Results in 1H'08**

Reported by Todd R. Younkin (Intel Corporation) in Litho Forum 2008

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(2) Acid amplified resists (High Yield Acids)

(3) EUV resists at 6.x nm (Future Problem)

Topics (1) Pulse radiolysis research on the detailed mechanisms of acid generation of chemically amplified EUV fluorinated polymer resists

Sadatatsu Ikeda[1,2], Kazumasa Okamoto[1,2], Hiroki Yamamoto[1,2], Akinori Saeki[1,2], Seiichi Tagawa[1,2], and Takahiro Kozawa[1,2]*

[1] *The Institute of Scientific and Industrial Research, Osaka University, 8-1 Mihogaoka, Ibaraki, Osaka 567-0047, Japan*
[2] *Japan Science and Technology Agency, CREST, c/o Osaka University, 8-1 Mihogaoka, Ibaraki, Osaka 567-0047, Japan*

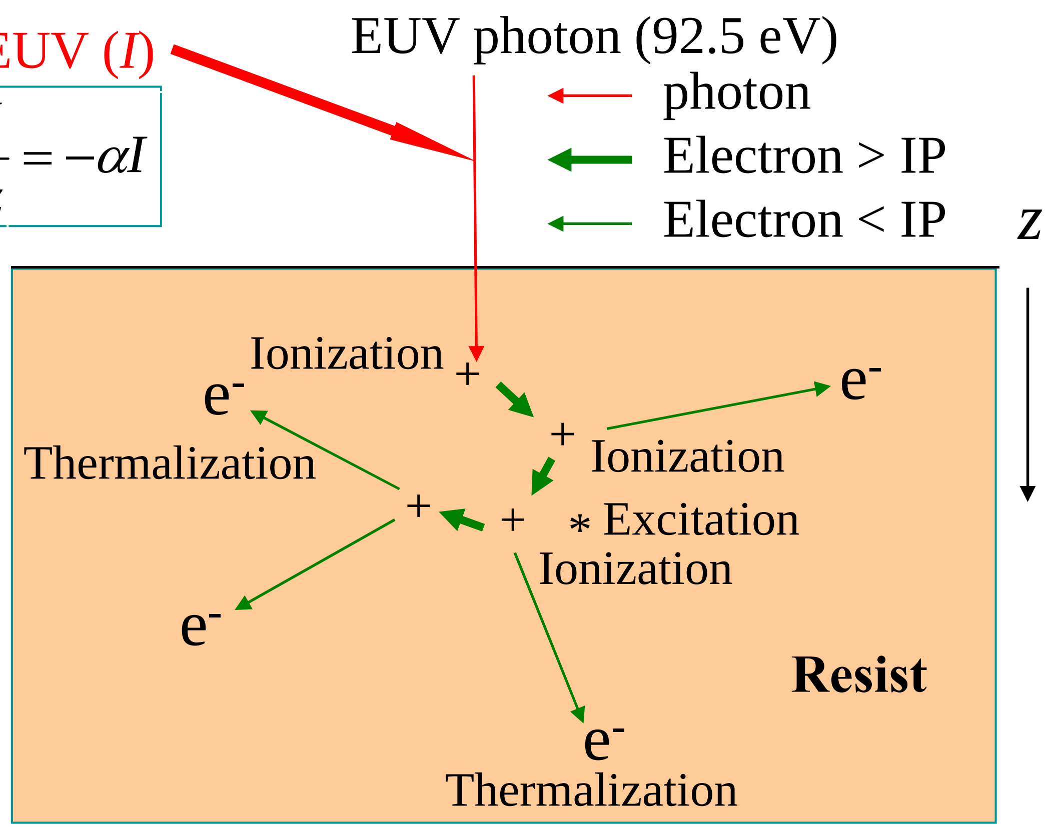
Interaction of EUV photon with CARs

Lambert's law

Intensity of EUV (I)

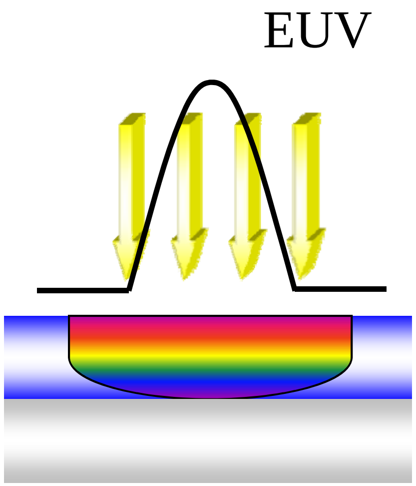
$$\frac{\partial I}{\partial z} = -\alpha I$$

Absorption coefficient (**α**)
PHS : 3.8 μm^{-1}



Absorption enhancement of incident energy

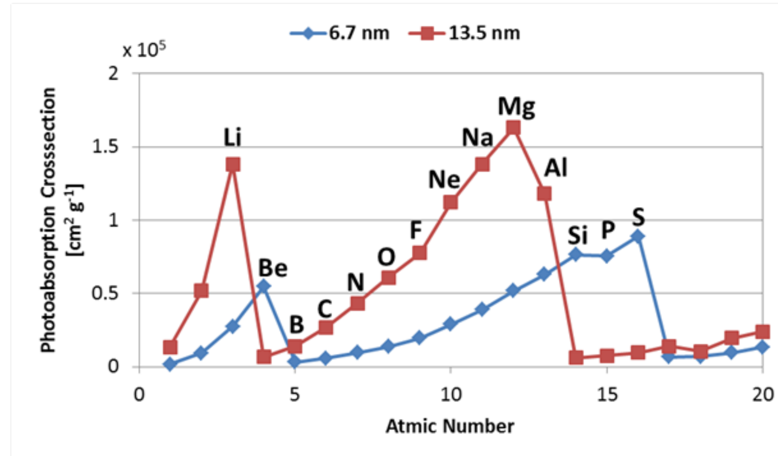
How to increase resist absorption



$$c(z)=\phi\left(-\frac{dI}{dz}\right)=\phi\alpha I_0 e^{-\alpha z}$$

c : acid concentration
ϕ : acid generation efficiency
α : absorption coefficient
I : light intensty
z : distance from the surface in depth direction

T. Kozawa et al., *J. Vac. Sci. Technol.* B24 (2006)L27.



NIST X-ray Attenuation Databases
http://www.nist.gov/pml/data/ffast/index.cfm

Fluorination of polymer

[H. Yamamoto et al. APEX 1 (2008) 047001.]

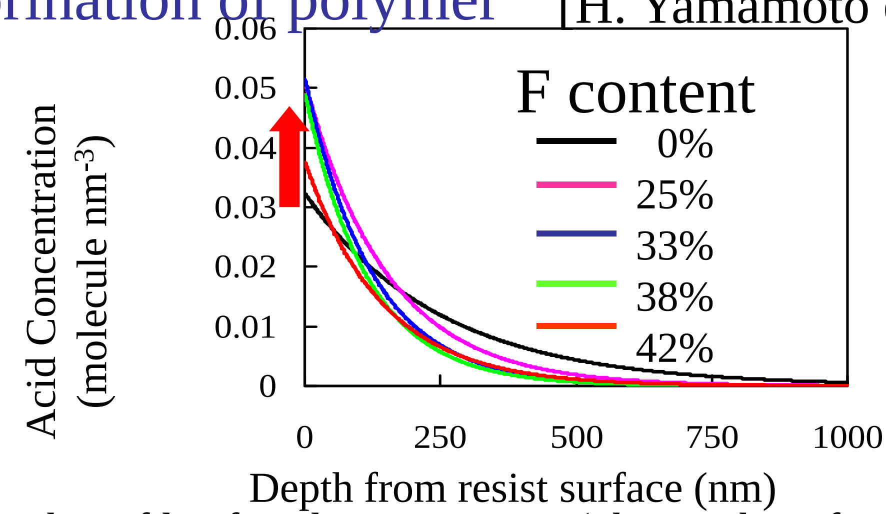


Fig. Depth profile of acid concentration (the number of molecules per unit volume) calculated with acid generation efficiency, absorption coefficient and the exposure dose of 5 mJ/cm^2.

Acid Generation Efficiencyφ and Absorption Coefficentα

Introduction of F atoms

F atoms increase cross sections.

α ↑

Increase in absorption coefficient

Acid yield ↑

T. Kozawa et al., *J. Vac. Sci. Technol.* B24 (2006) L27.

F atoms interfere with acid generation.

ϕ ↓

Decrease in acid generation efficiency per photon

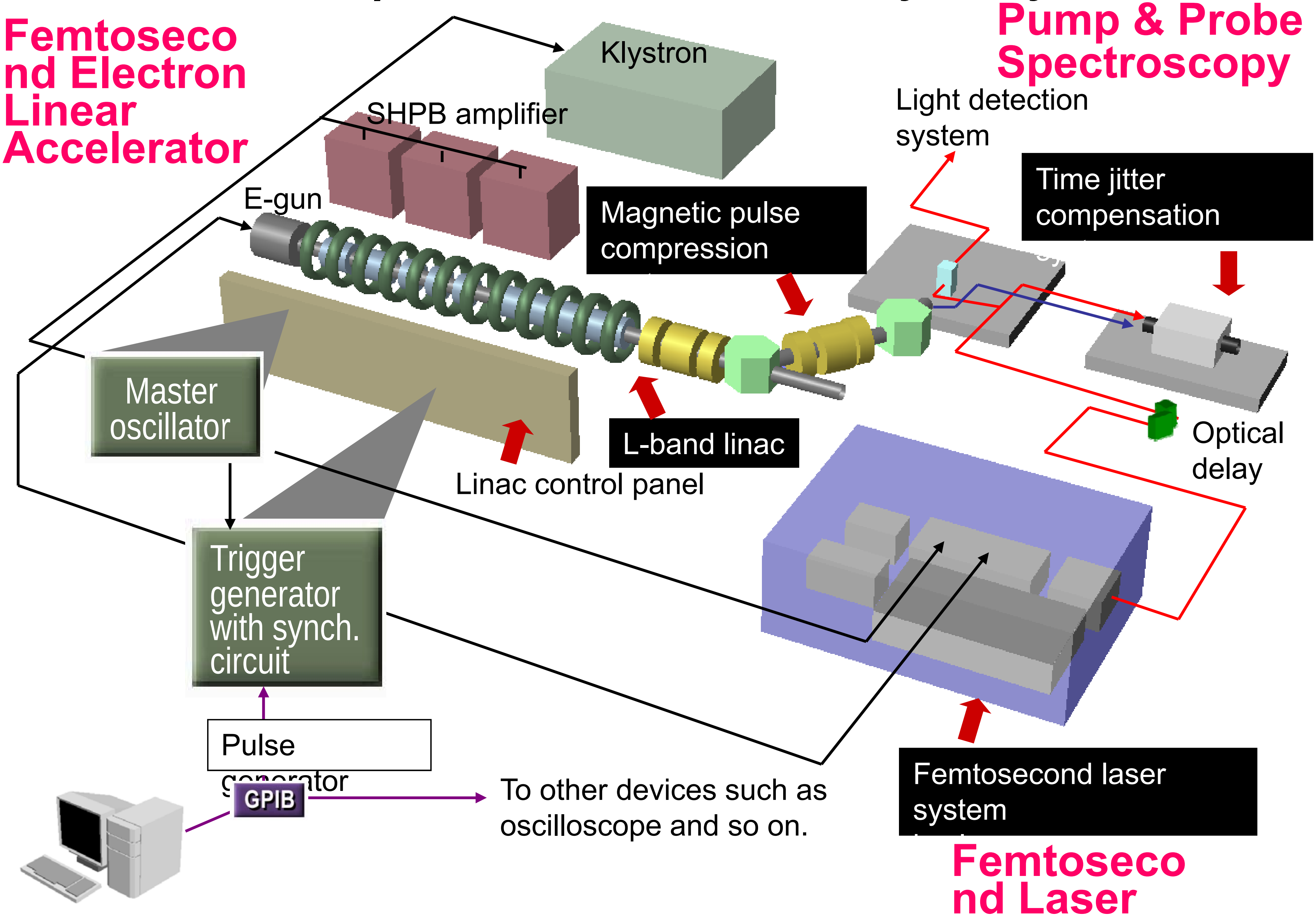
Acid yield ↓

H. Yamamoto et al . *J. Vac. Sci.* Technol. 24 (2006) 1833

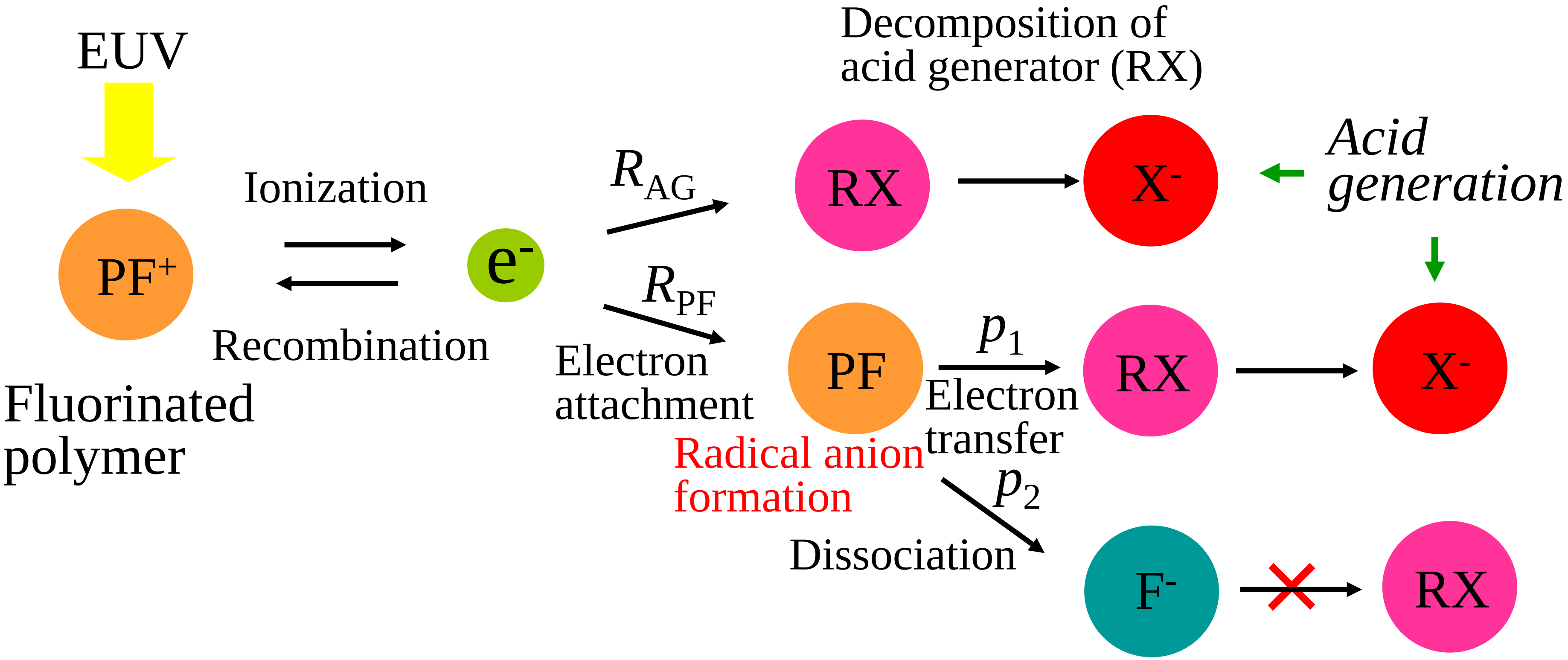
Understanding of acid generation mechanisms and synthesizing new chemical structures of fluorinated polymer resists are important in enhancement of acid generation.

General: Ultra thin resists, increase in PAG concentrations, etc.

Subpicosecond Pulse Radiolysis System



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

Virtual effective reaction radius, R_p

$$R_p = p_2 R_{PF}$$

Radiation Chemistry of Fluorinated Aromatic Compounds

8FN ラジカルアニオン

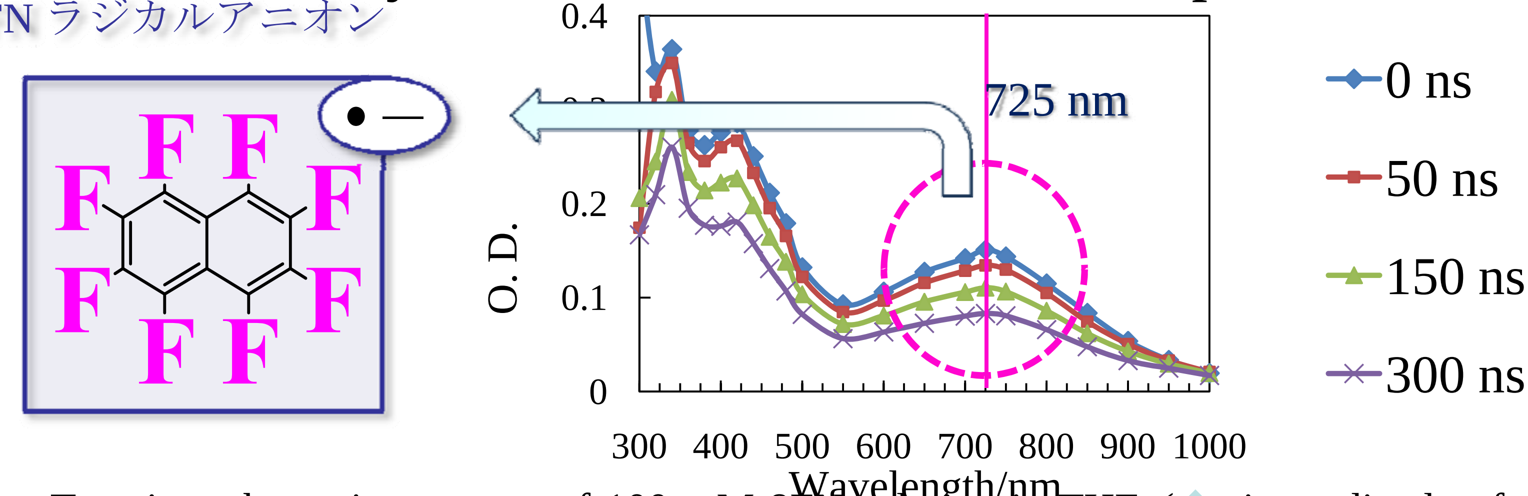


Fig. Transient absorption spectra of 100 mM 8FN solution in THF. (◆; immediately after the pulse(0 ns) ■; 50 ns ; 150 ns ×; 300 ns).

1FN ラジカルアニオン

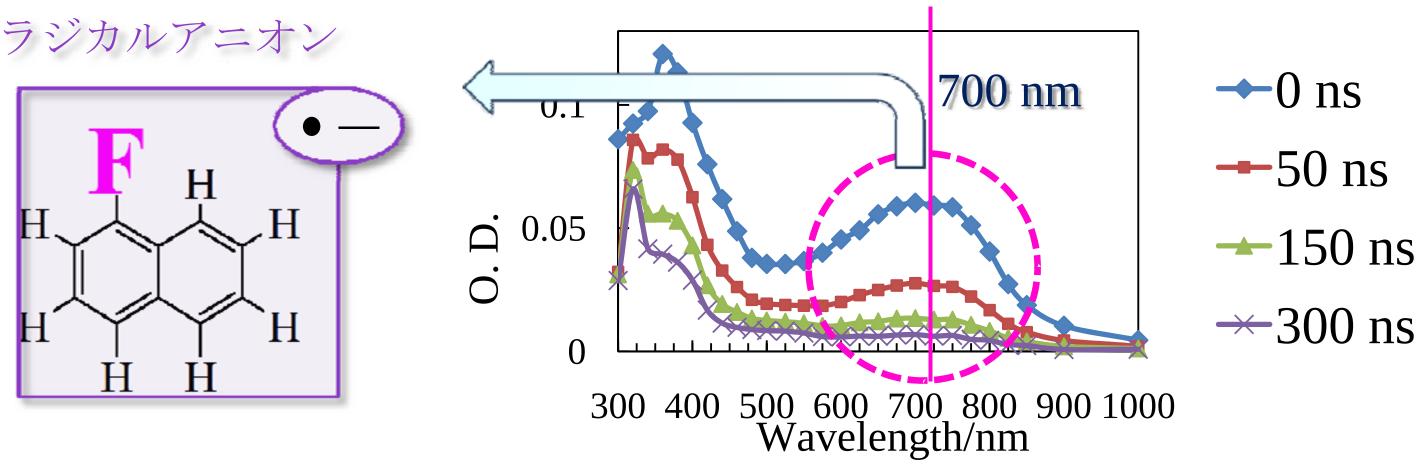


Fig. Transient absorption spectra of 100 mM 1FN solution in THF. (◆; immediately after the pulse(0 ns) ■; 50 ns ; 150 ns ×; 300 ns).

Both acid generation efficiency φ and absorption coefficent α of 8FN are larger than those of 1FN.

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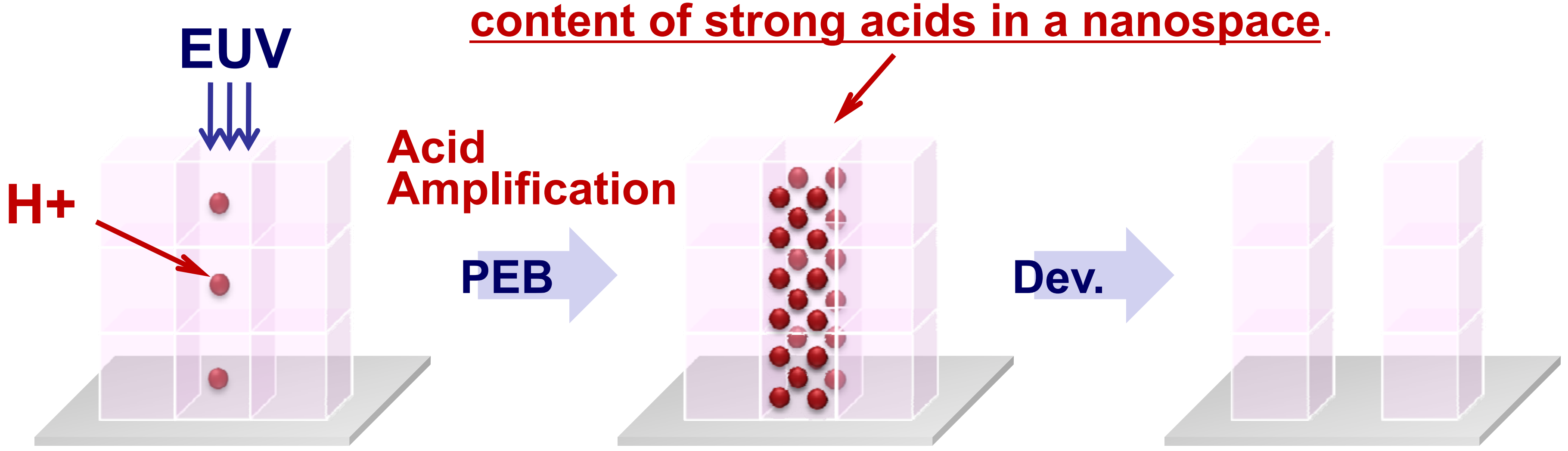
Topics (2) Acid Amplification Reaction for Sensitivity Enhancement of EUV Resists: A Pulse Radiolysis Study

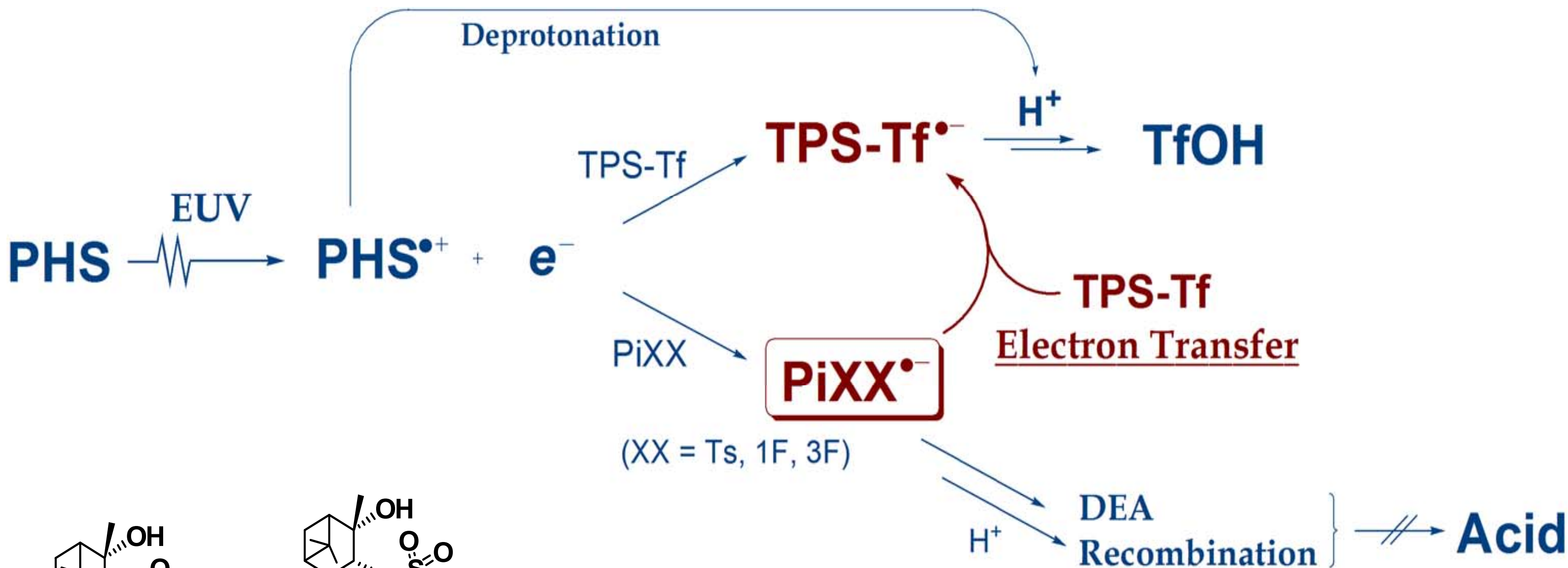
K. Enomoto,[1,2] K. Arimitsu,[3] A. Yoshizawa,[3] H. Yamamoto,[1,2] A. Oshima,[1] T. Kozawa,[1,2] and S. Tagawa[1,2]

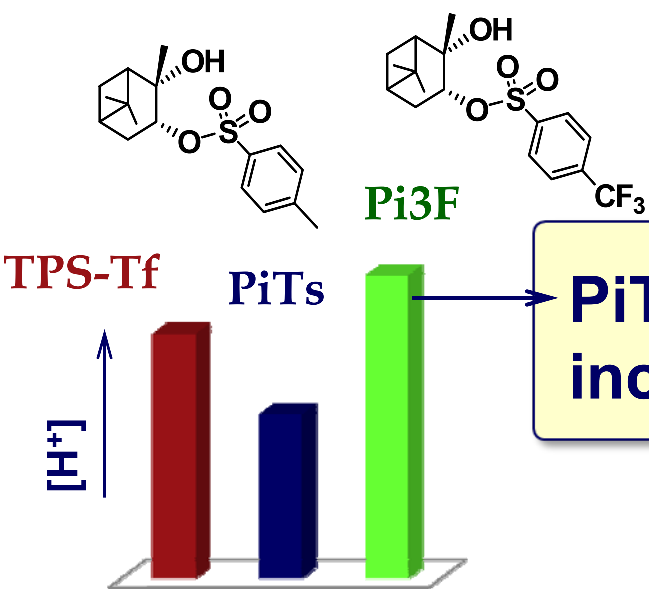
1) The ISIR, Osaka University, 2) CREST/JST, 3) Tokyo University of Science

The high sensitivity of EUV resists is strongly required. Acid amplification produces **high content of strong acids in a nanospace**.



The Acid Production Pathway

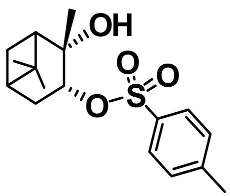


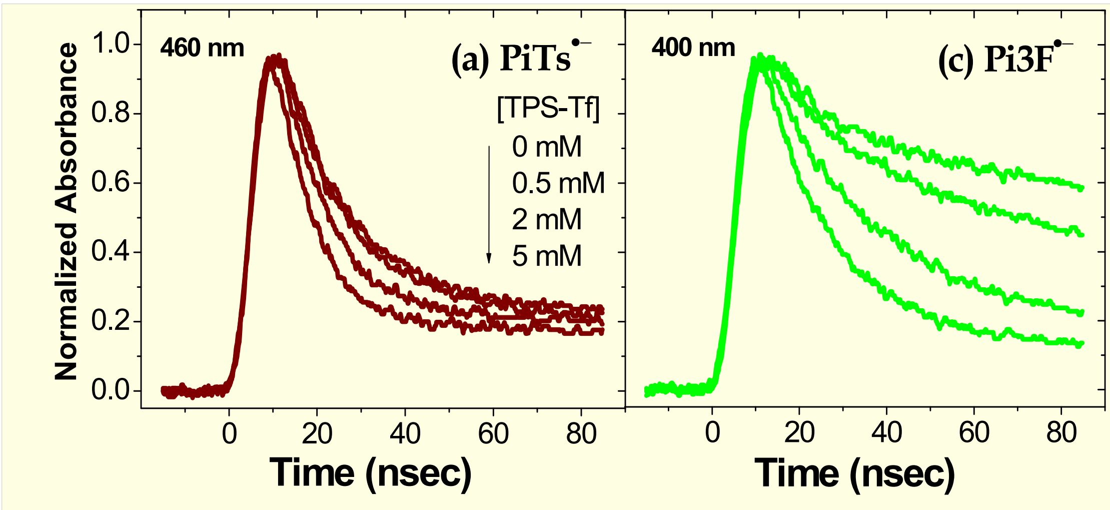


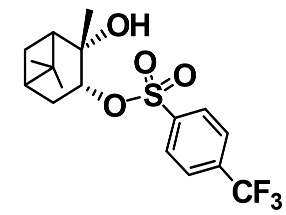
PiTs decreases acid yield, but Pi3F increases acid yield.

Electron Transfer to TPS-Tf

Pi3F•− + TPS-Tf → TPS-Tf•− + Pi3F (S_0)







The long-lived Pi3F•− radical anions efficiently undergoes the electron transfer to TPS-Tf to form TPS-Tf•−, which then decomposes to generate TfOH.

Good acid amplifiers are quite important in increasing acid generation

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Topics (3)

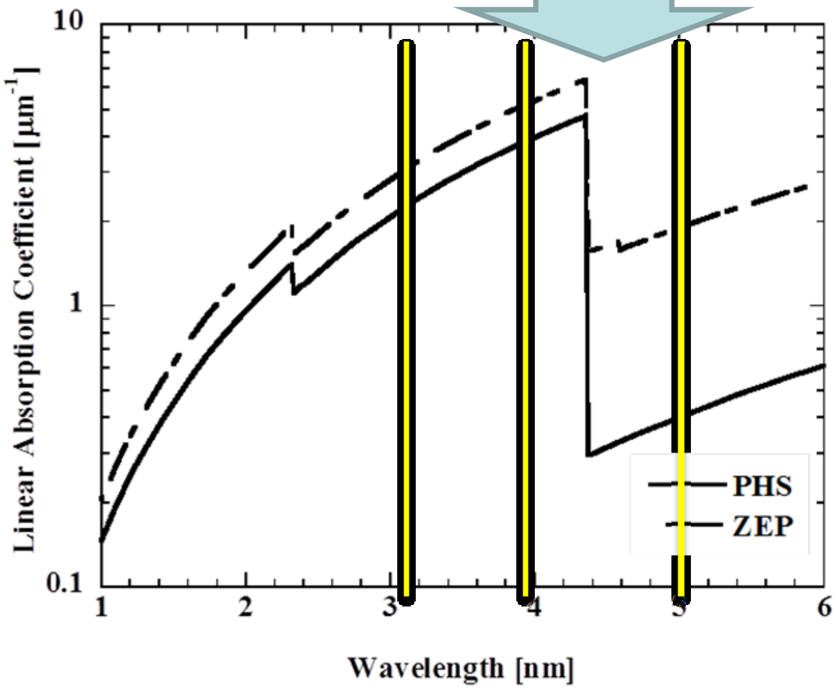
Extendibility of EUV resists in the exposure wavelength from 13.5 down to 3.1 nm for next-generation lithography

Tomoko Gowa Oyama*, Tomohiro Takahashi*,
Akihiro Oshima#, Masakazu Washio*
and Seiichi Tagawa*#+
***RISE, Waseda Univ., Japan, #ISIR, Osaka Univ., Japan, +JST/CREST,c/o Osaka University**

Experimetal Results on Resist Sensitivities

Obtained sensitivities (E_0) of the resist materials for each EUV/soft X-ray source.

Wavelength [nm]	E_0 [mJ/cm^2] TDUR-P722	ZEP520A	ZEP7000
3.1	2.5	11	1.0
3.9	1.9	9.0	0.60
5.0	9.6	17	1.4



Absorbed Dose

$$D_0 = \alpha E_0 \int \exp(-\alpha T)\, dT$$

α: absorption coefficient

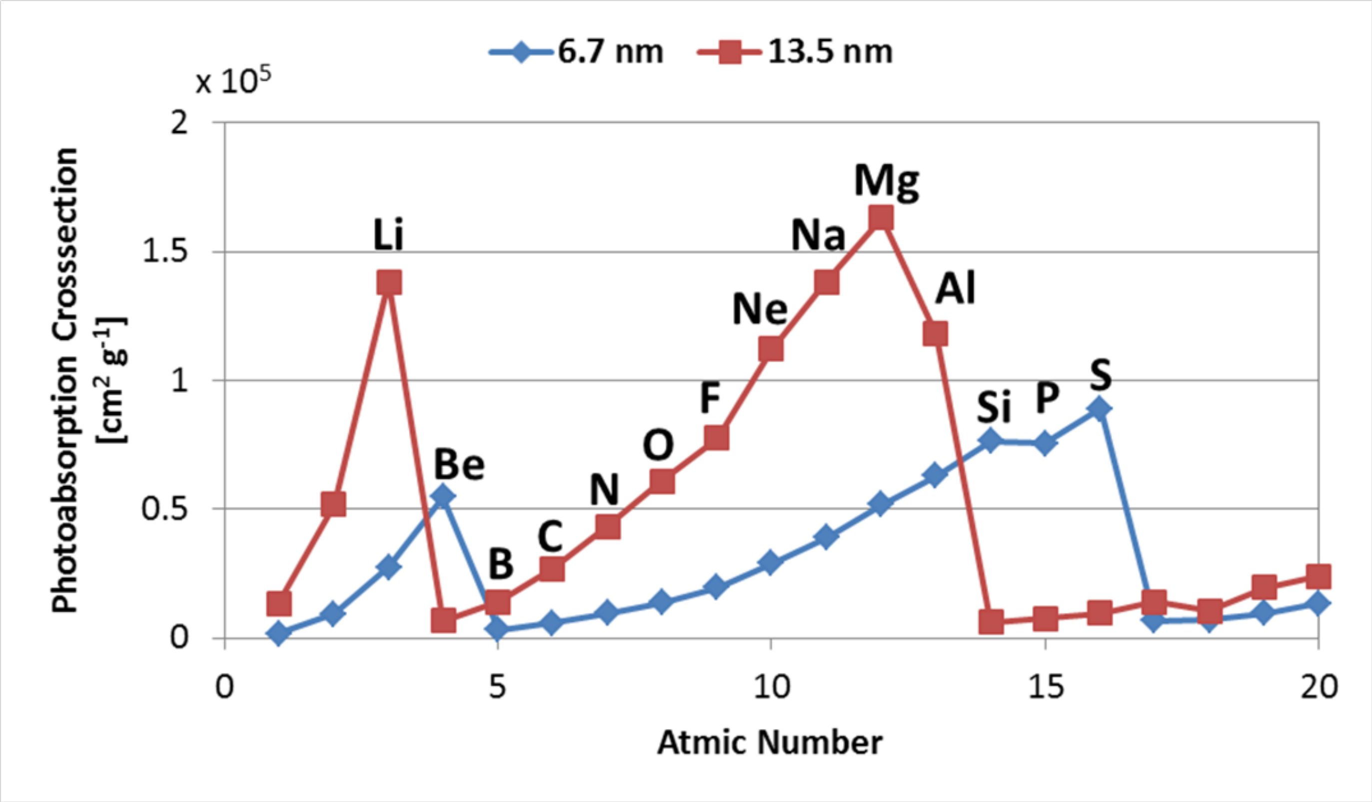
T: resist thickness

Wavelength [nm]	D_0 [kGy=J/g] TDUR-P722 600 nm-thick	ZEP520A 350 nm-thick	ZEP7000 150 nm-thick
3.1	15	45	2.3
3.9	14 ~15	47 ~ 48	2.1 ~2.2
5.0	17	51	2.2

Coclusion: 1. Absorbed doses (Gy: Gray, J/kg) are almost constant for each resist.

2. E_0 (mJ/cm^2) is scattered and determined by linear absorption coefficients.

Photoabsorption Crosssection at 6.7 nm and 13.5 nm



NIST X-ray Attenuation Databases http://www.nist.gov/pml/data/ffast/index.cfm

Linear absorption coefficient = Density x Photoabsorption cross section

Conclusion of Topics (3)

1. Each resist material would have its particular value of the absorbed dose (Gray: J/kg) for pattern formation, regardless of the exposure wavelengths in the range of EUV/soft X-rays from 13.5 to 3.1 nm. In other words, this result suggested that the linear absorption coefficient would be the major factor for determination of the exposure wavelength dependence of resist sensitivity (mJ/cm^2), although there are other minor important factors such as energies of the secondary electrons, that is, thermalization length and initial configuration of reactive intermediates (multi-spur effects).

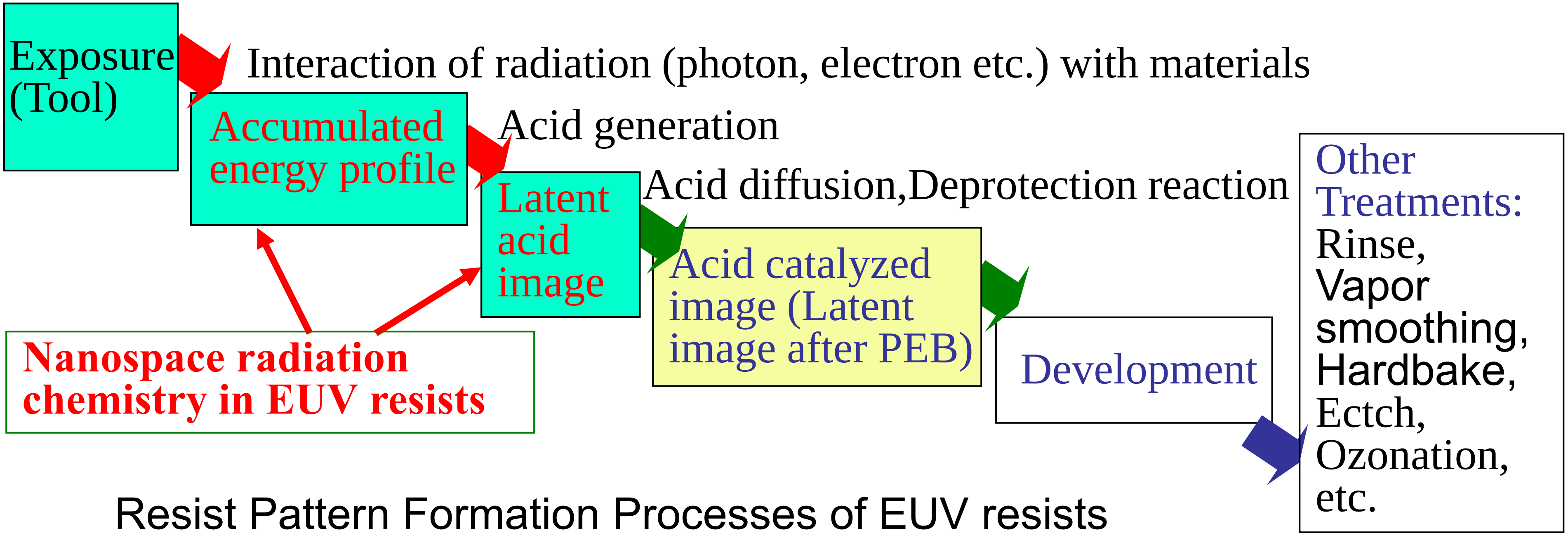
2. If resist sensitivity to a certain wavelength is obtained, the sensitivities to other wavelengths could be roughly estimated with respective linear absorption coefficients in the range of EUV/soft X-rays. At 6.7 nm exposure, resists containing S, P, and Si atoms have large linear absorption coefficients.

Linear Absorption Coefficient [μm^{-1}]

Wavelength [nm]	PHS	ZEP	S	a-Si	HSQ	PSQ	PMPS
13.5	3.7	4.6	2.0	1.4	4.4	4.2	6.5
6.7	0.83	1.1	19	18	6.5	3.6	5.5

hydrogen silsesquioxane, (HSQ, 1.4 g cm^{-3}), poly(2-methyl-1-pentenesulfone) (PMPS, 2.2 g cm^{-3})

Conclusion



The improvement at each stage is required cloth to its physical and chemical limit. The good integration of improvement at each stage is strongly needed for the development of next generation EUV resists. Especially understanding nanospace radiation chemistry is important and essential in the development of high performance EUV resists.

THANK YOU FOR YOUR KIND ATTENTION.