Modelling of Chemically Amplified EUV Resist Processes

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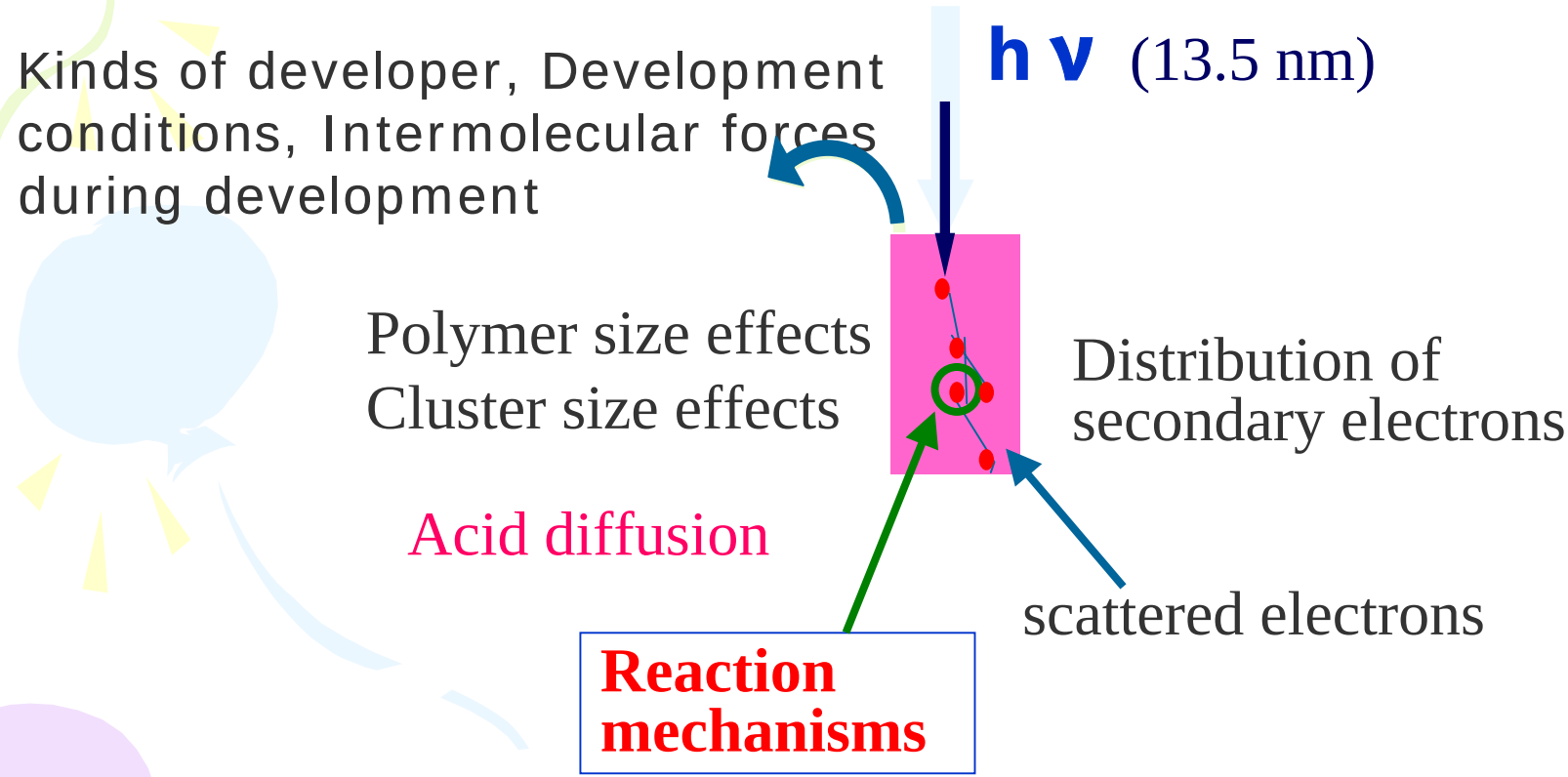
Requirements for EUV Resists

1.sensitivity, 2.space resolution, 3.LER, 4.shot noise

Without understanding the details of the reaction mechanisms of chemically amplified resists, it is impossible to develop EUV resists which meet the strict requirements for mass production.

Sensitivity
and
Nanoscale Topology of Resist Patterns

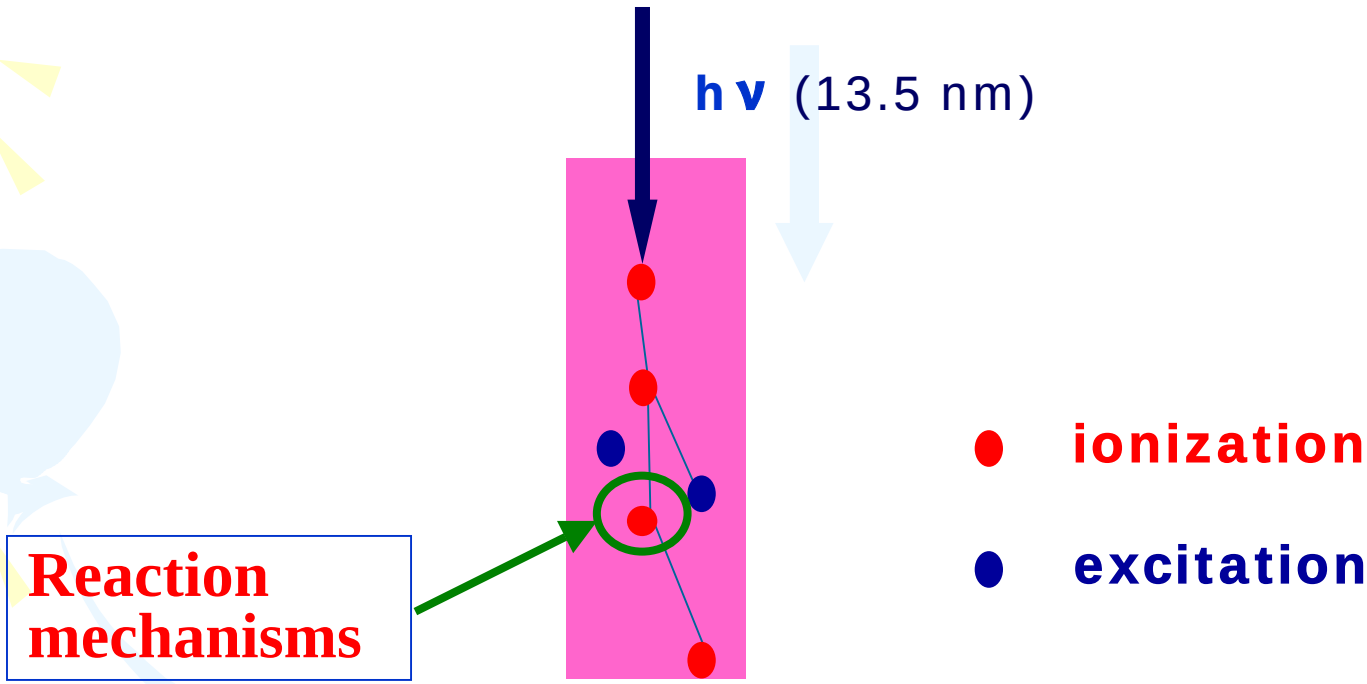


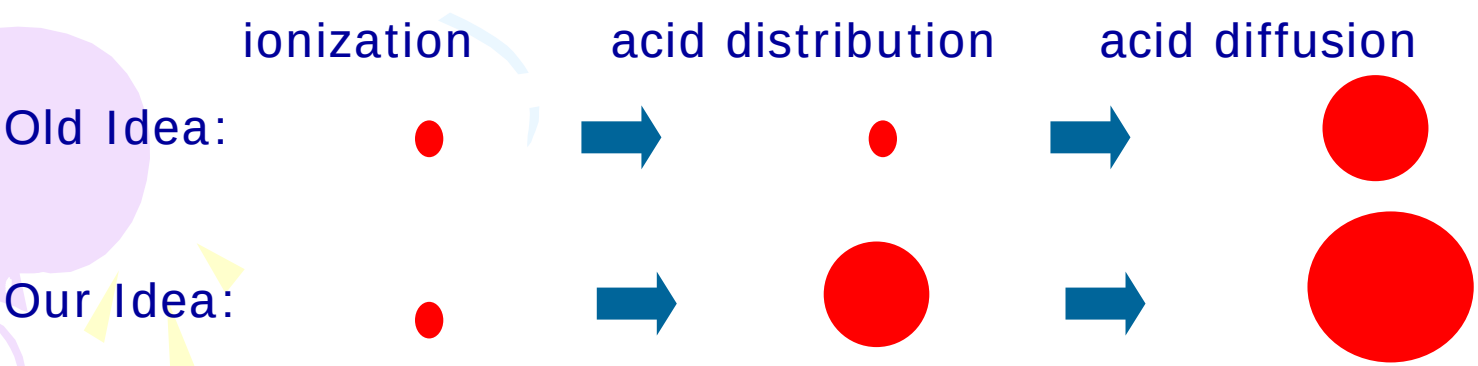
EB can be focused less than 1 nm. However, technical barriers exist around 30 nm for mass production type resist patterns. Why?

Energy deposition point and reaction point are different.

One EUV Light: ● **Ionization:4~6**, ● **Excitation:1~2**

Acid generation yields: 1~3



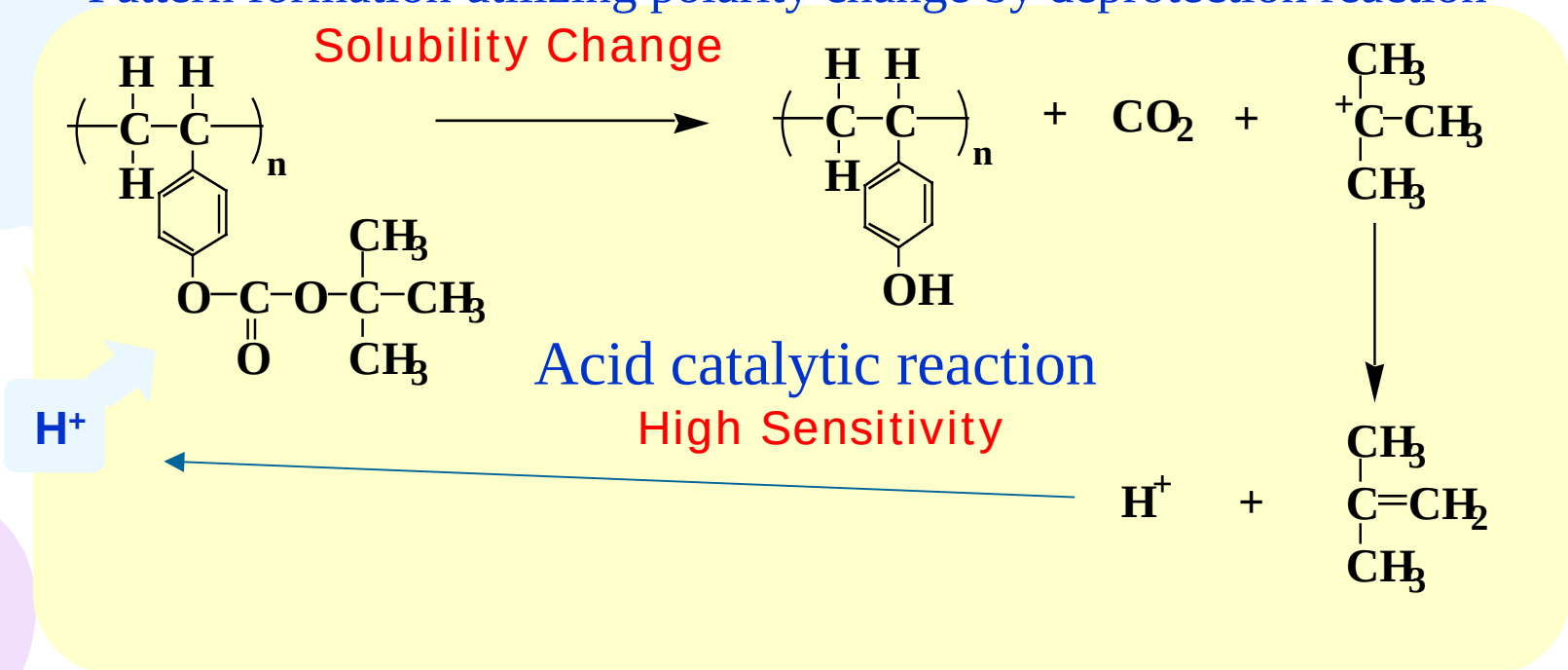


Chemically amplified resist

Generation of acid by exposure

$$Ph_3S^+X^- \xrightarrow{h\nu,\ \text{radiation}} H^+X^-$$

Pattern formation utilizing polarity change by deprotection reaction



×Polmerization, graft polmerization, and others

Acid Generation Reaction Mechanism Induced by Ionizing Radiation in Triphenylsulfonium triflate Solution

Through Ionization of Base Polymer (95%)

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

$$RH^{+\cdot} + e^- \xrightarrow{RH} R\cdot + RHH^+ + e^-$$

$$Ph_3S^+X^- \xrightarrow{e^-} Ph_2S + Ph\cdot + X^-$$

$$Ph_2S + Ph\cdot + X^- \xrightarrow{H^+} Ph_2S + PhH + H^+X^-$$

1.99 (95%)

Through Excited States of Sulfonium Salts (5%)

$$(Ph_3S^+X^-)^* \xrightarrow{\text{Homolysis}} Ph_2S^{+\cdot} + Ph\cdot + X^-$$

$$(Ph_3S^+X^-)^* \xrightarrow{\text{Heterolysis}} Ph_2S + Ph^+ + X^-$$

in-cage

$$Ph_2S^{+\cdot} + Ph\cdot + X^- \xrightarrow{RH:\ \text{Solvent}} Ph_2S + PhH + H^+X^-$$

cage-escaped

0.040 (1.9%)

in-cage Reconbination

$$Ph_2S^{+\cdot} + Ph\cdot + X^- \rightarrow o\text{-PhPhSPh} + H^+X^-$$

0.010 (0.46%)

$$Ph_2S^{+\cdot} + Ph\cdot + X^- \rightarrow m\text{-PhPhSPh} + H^+X^-$$

0.0012 (0.06%)

$$Ph_2S + Ph^+ + X^- \rightarrow p\text{-PhPhSPh} + H^+X^-$$

0.0034 (0.16%)

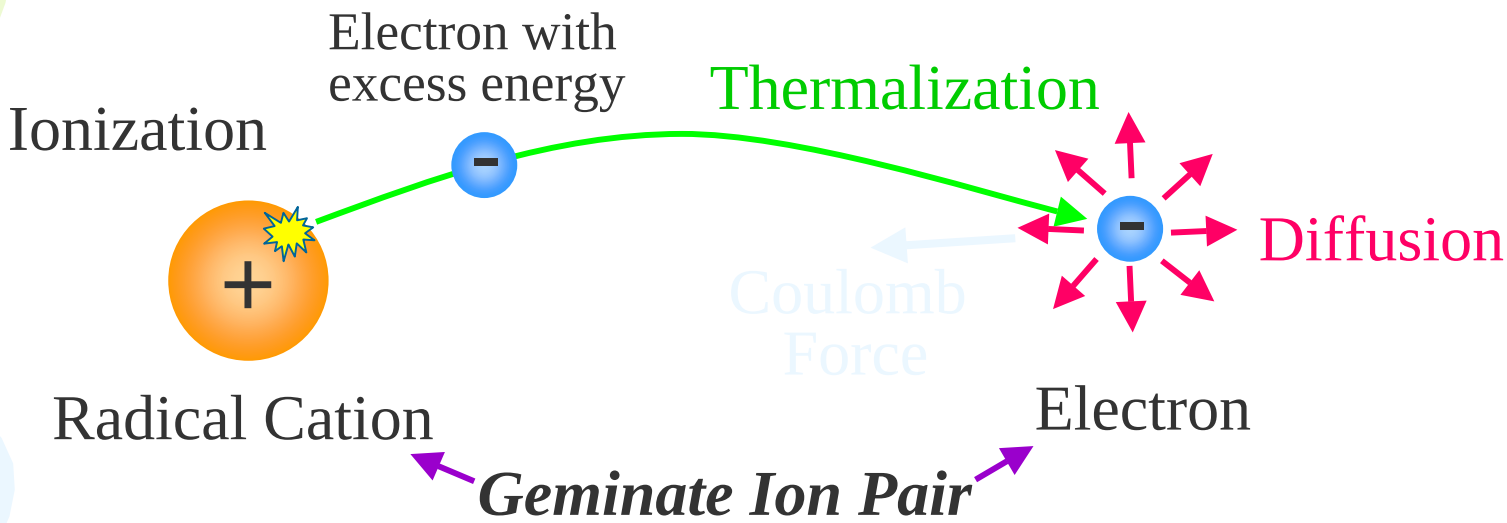
in-cage

$$Ph_2S + Ph^+ + X^- \xrightarrow{RH} Ph_2S + PhR + H^+X^-$$

cage-escaped

0.054 (2.6%)

Electron dynamics in early processes of radiation chemistry



Smoluchowski equation

$$\frac{\partial w}{\partial t} = D\nabla\left(\nabla w + w\frac{1}{k_B T}\nabla V\right)$$

w : Probability density of electrons
$\boldsymbol{k_B}$: Boltzmann constant
V : Coulomb potential
T : Absolute temperature
D : Sum of diffusion coefficient

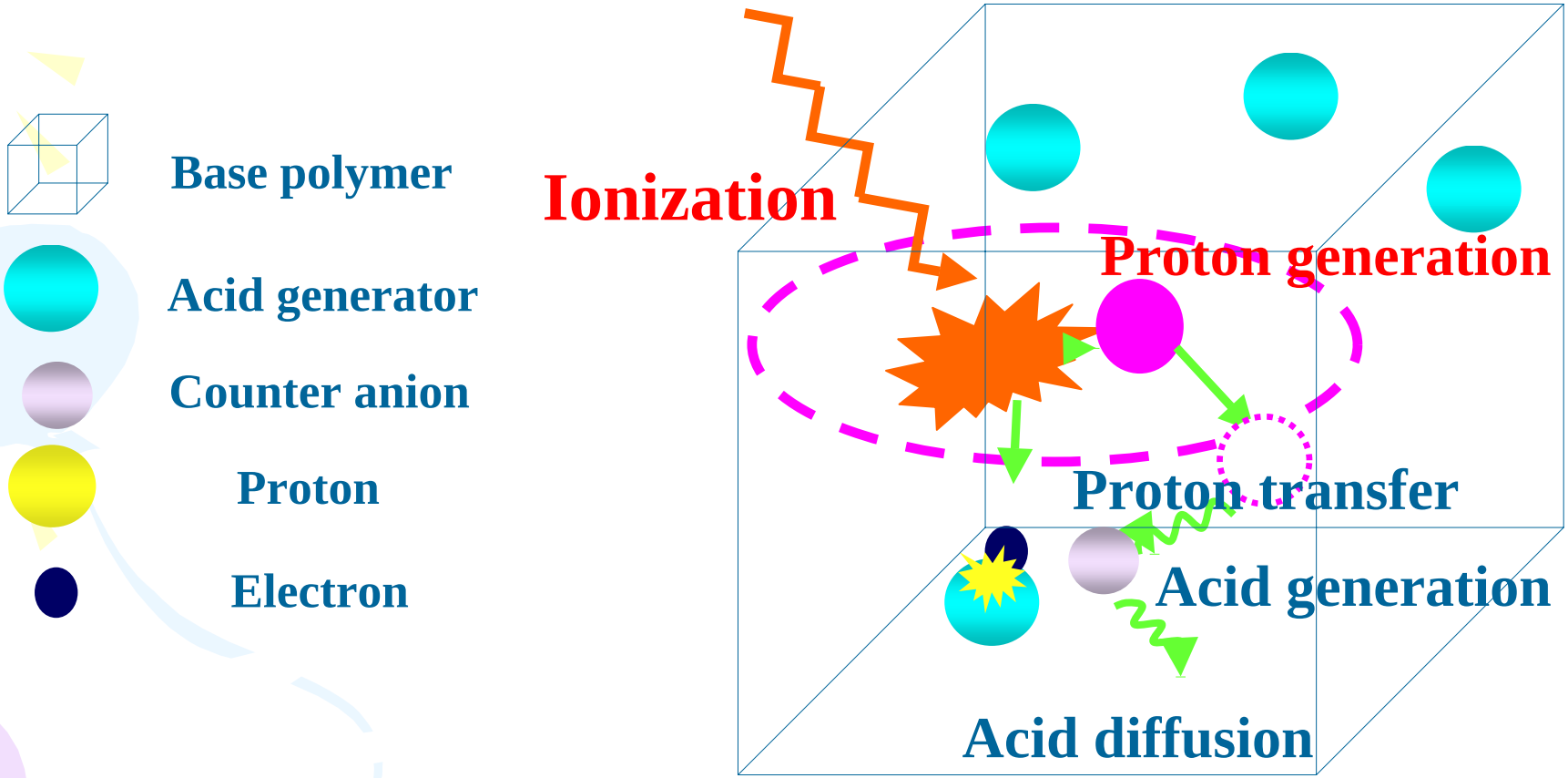
Initial distribution function

$$f(r, r_0) = \frac{1}{r_0}\exp\left(-\frac{r}{r_0}\right)$$

r : Distance between radical cation and electron
$\boldsymbol{r_0}$: Initial separation distance on average

Acid generation mechanism – Ionization channel

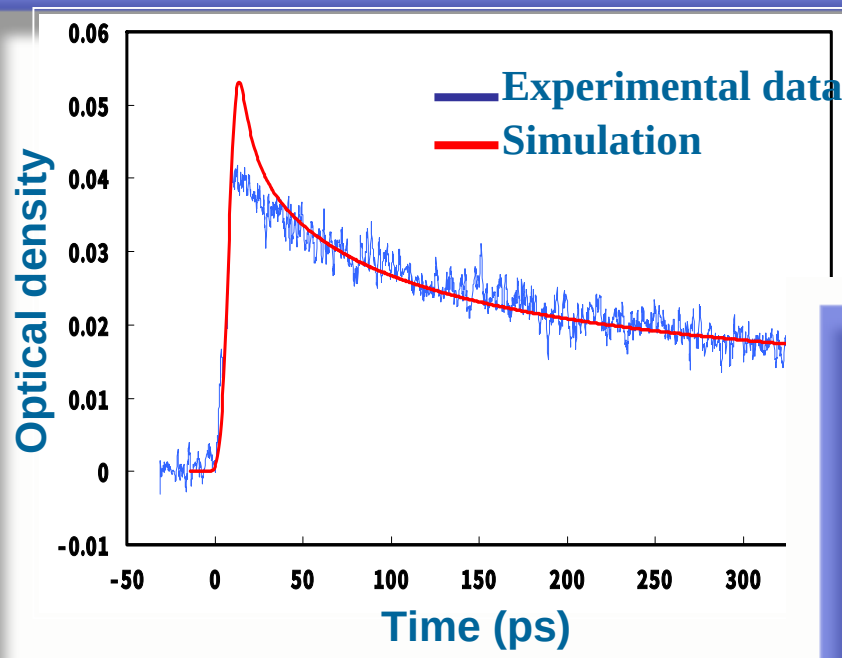
Electron beam, X-ray, EUV



Reaction control in nanospace --Time space translation

A. Saeki et al. Jpn. J. Appl. Phys. 41 (2002) 4213.

It is essential to minimize the displacement between energy deposition point and reaction point.



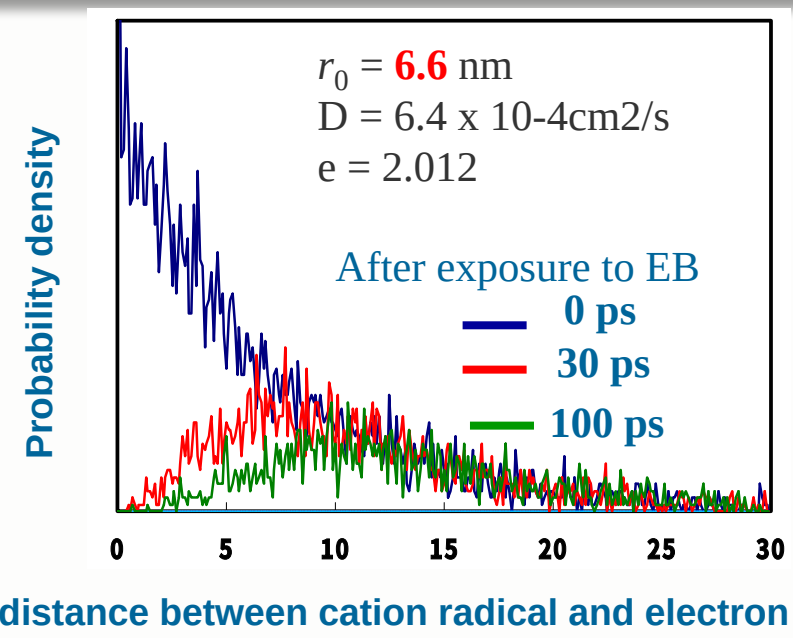
Experimental data obtained in the femtosecond pulse radiolysis and simulation

Spatial separation between electron and cation radical causes the displacement between energy deposition point and reaction point. For the nanotechnology, it is essential to decrease the displacement.

Time-space translation

Translation of picosecond temporal data to nanometer spatial data

(So far, available only at ISIR)



Change of distance between electron and cation radical generated by electron beam irradiation.

Formulation

The reaction of acid generators with electrons:

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

Effective reaction radius of acid generators:

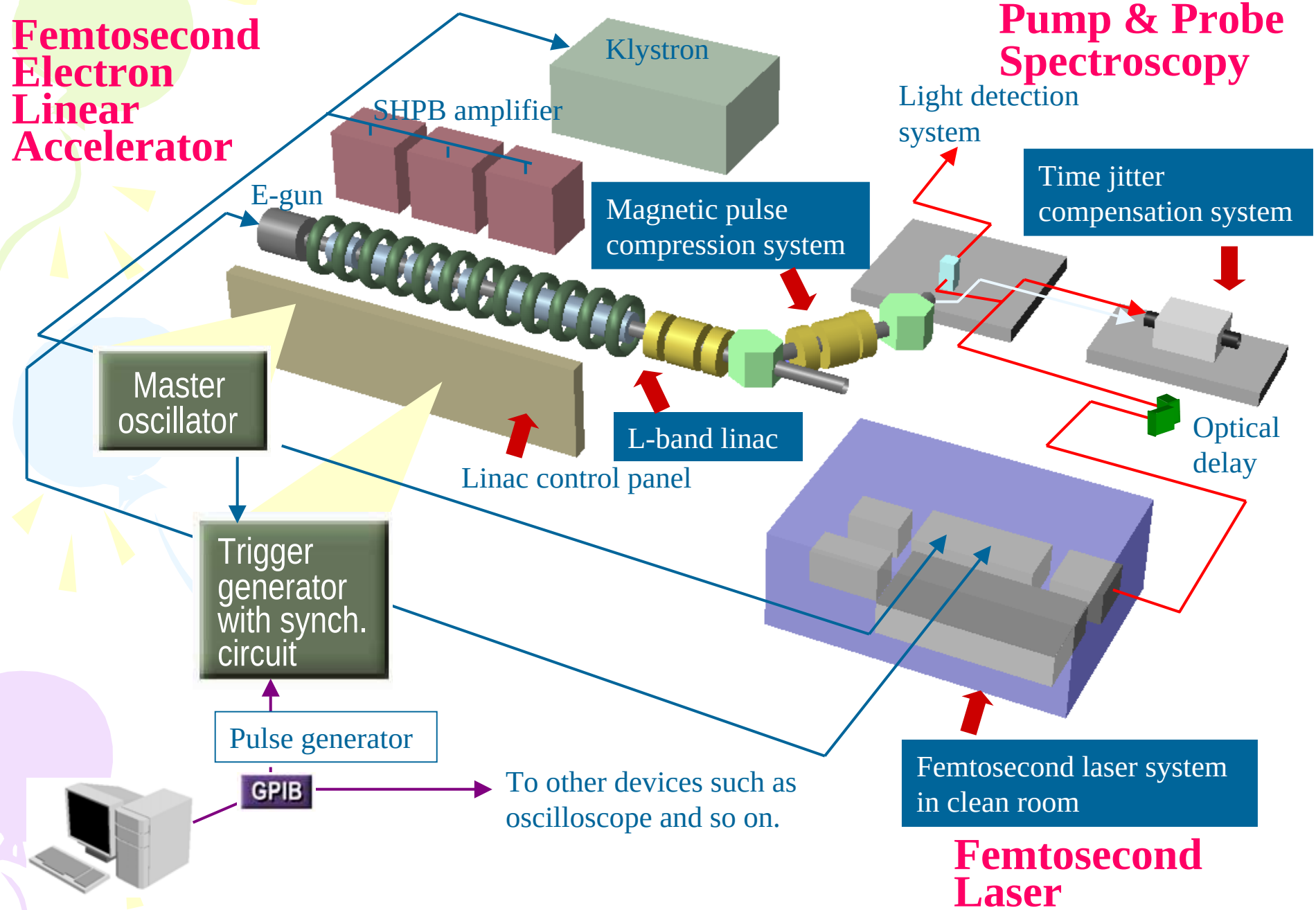
$$k = 4\pi RD$$

Electron dynamics in resist materials:

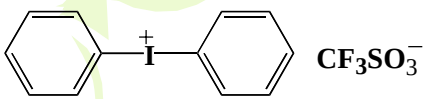
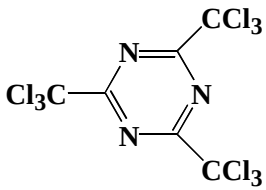
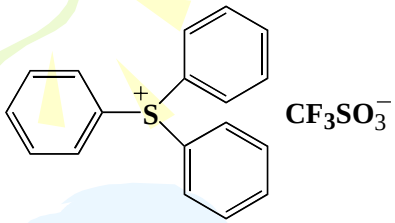
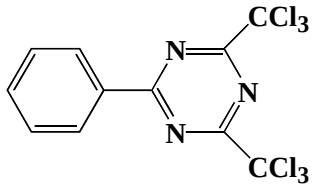
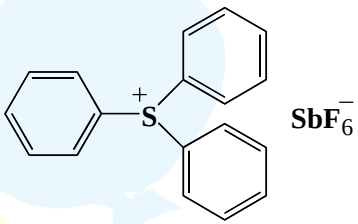
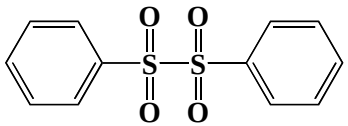
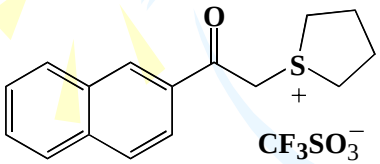
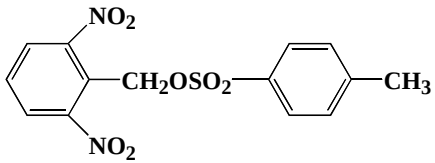
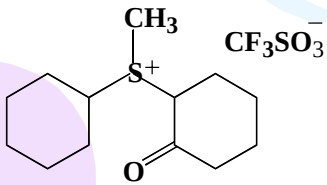
$$\frac{\partial w}{\partial Dt} = \nabla\left(\nabla w + w\frac{1}{k_B T}\nabla V\right) - 4\pi RCw$$

w : probability density of electrons
k : rate constant of reaction of acid generator with electrons
C : concentration of acid generators
R : effective reaction radius

Subpicosecond Pulse Radiolysis System



Effective reaction radii of acid generators

Acid generator	k ($M^{-1}s^{-1}$)	R (nm)	Acid generator	k ($M^{-1}s^{-1}$)	R (nm)
	2.4×10^{10}	**2.1**		2.2×10^{10}	**1.9**
	2.7×10^{10}	**2.4**		2.5×10^{10}	**2.2**
	2.5×10^{10}	**2.2**		1.1×10^{10}	**0.96**
	1.9×10^{10}	**1.7**		2.2×10^{10}	**1.9**
	1.6×10^{10}	**1.4**			

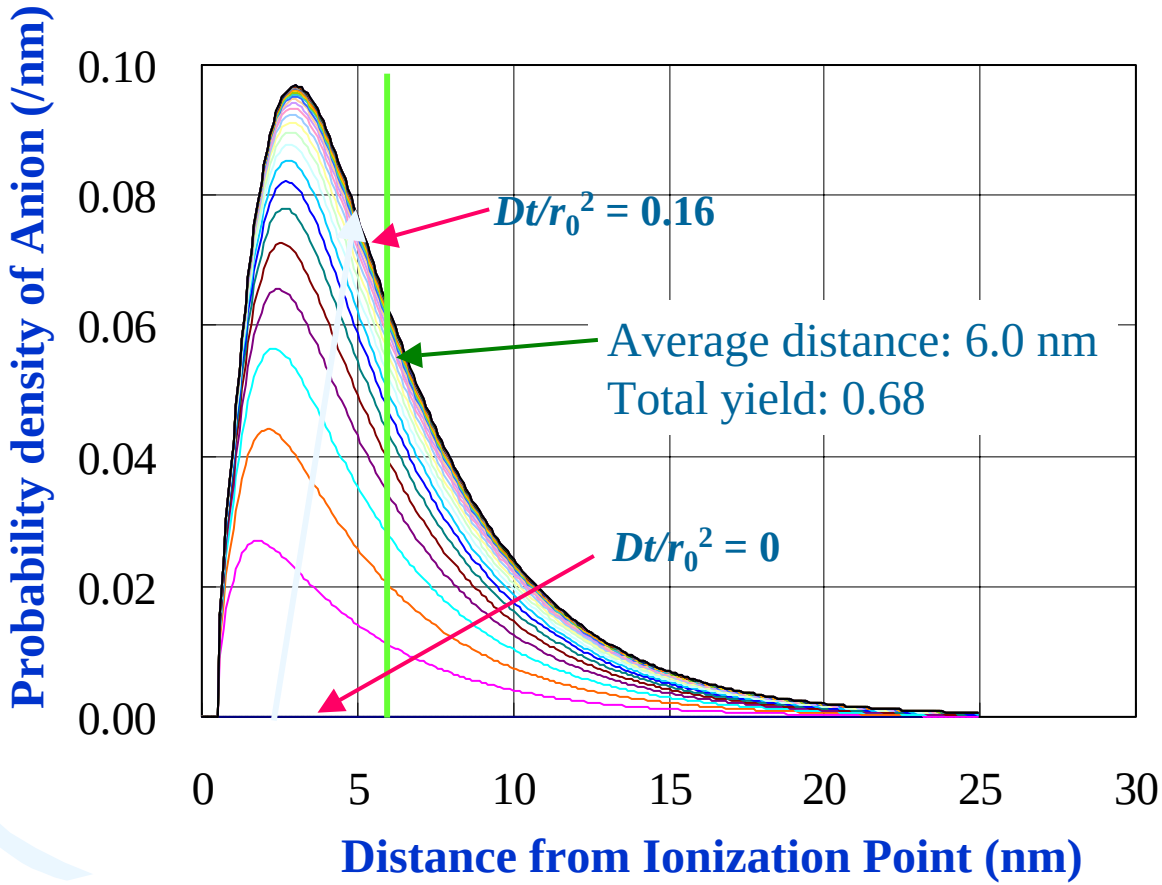
$$k = 4\pi RD$$

R : Effective reaction radius of acid generators

D : Diffusion coefficient of solvated electrons in methanol (1.5×10^{-9} m^2s^{-1})

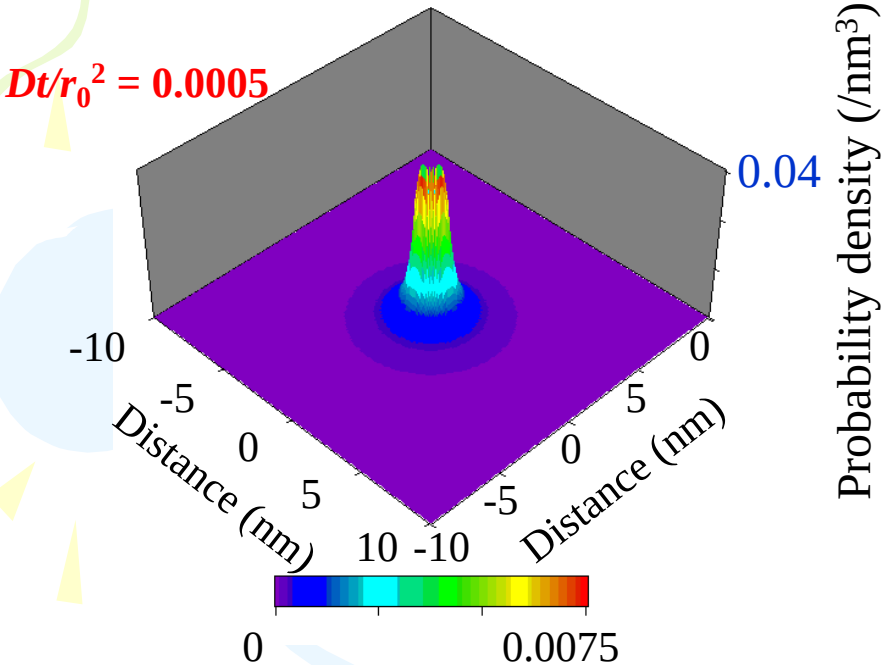
k : Rate constant of reaction of acid generators with solvated electron in methanol

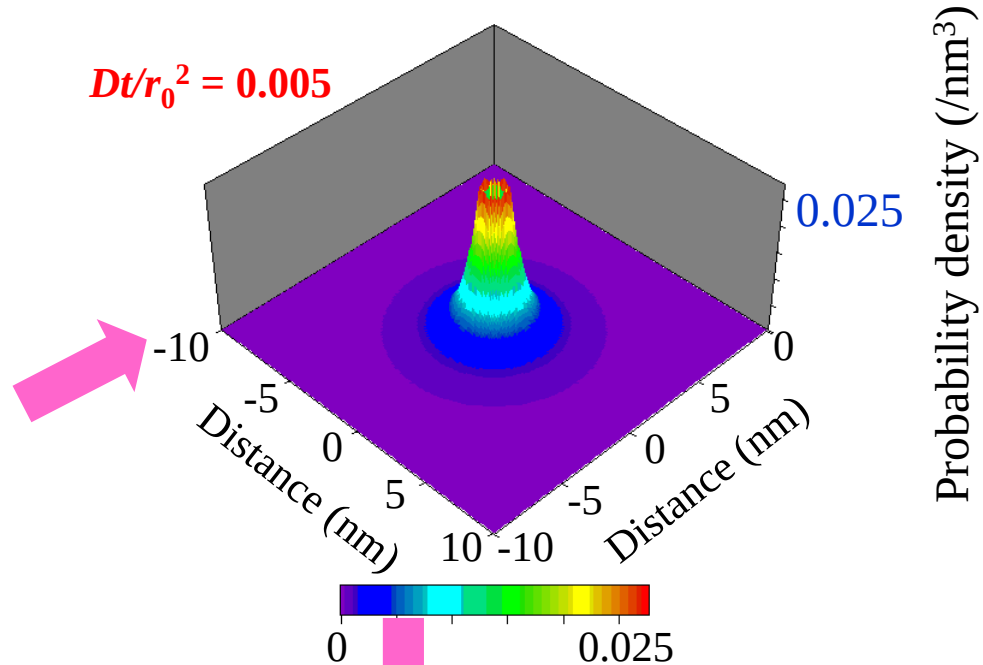
The evolution of counter anion distribution

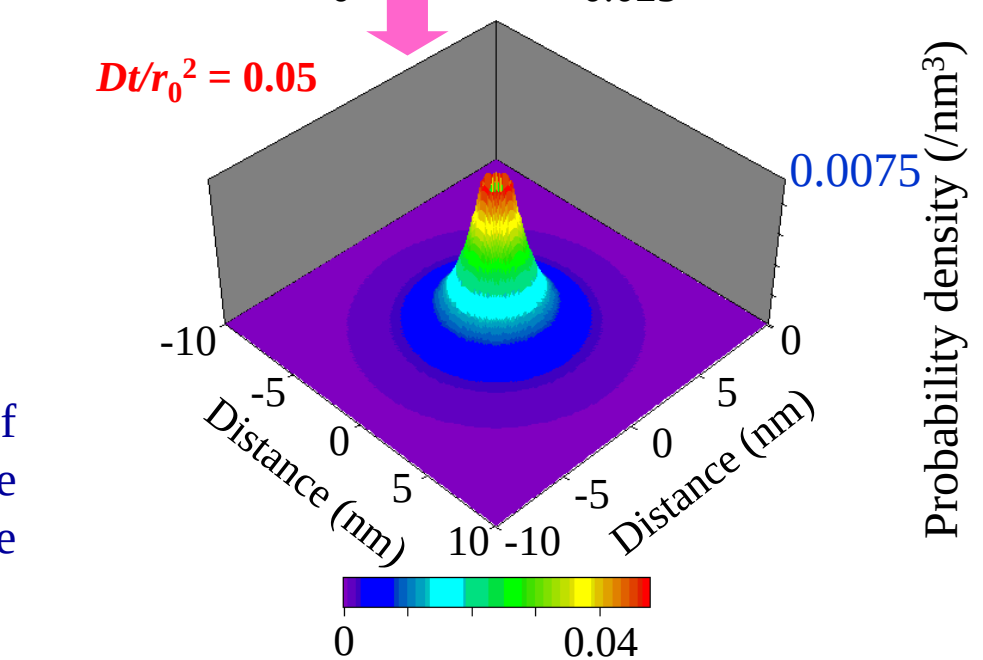


. The evolution of counter anion distribution calculated with the parameters: the concentration of acid generator, C = 5 wt. %, the initial separation distance, r_0 = 4 nm, the dielectric constant, ε = 4, the effective reaction radius, R = 2.4 nm. Dt/r_0^2 is a non-dimensional parameter and represents time. The vertical axis represents the probability density of electrons per unit distance. The probability is spherically integrated. The time step ($\Delta Dt/r_0^2$) between each line is 0.005 and the maximum time (Dt/r_0^2) is 0.16.

Counter anion distribution around ionization point

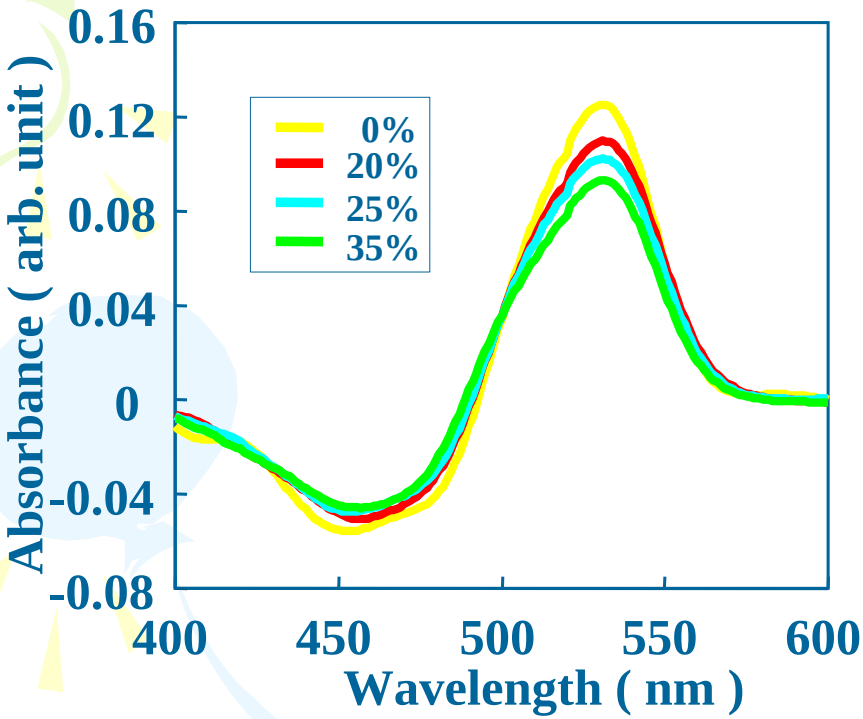


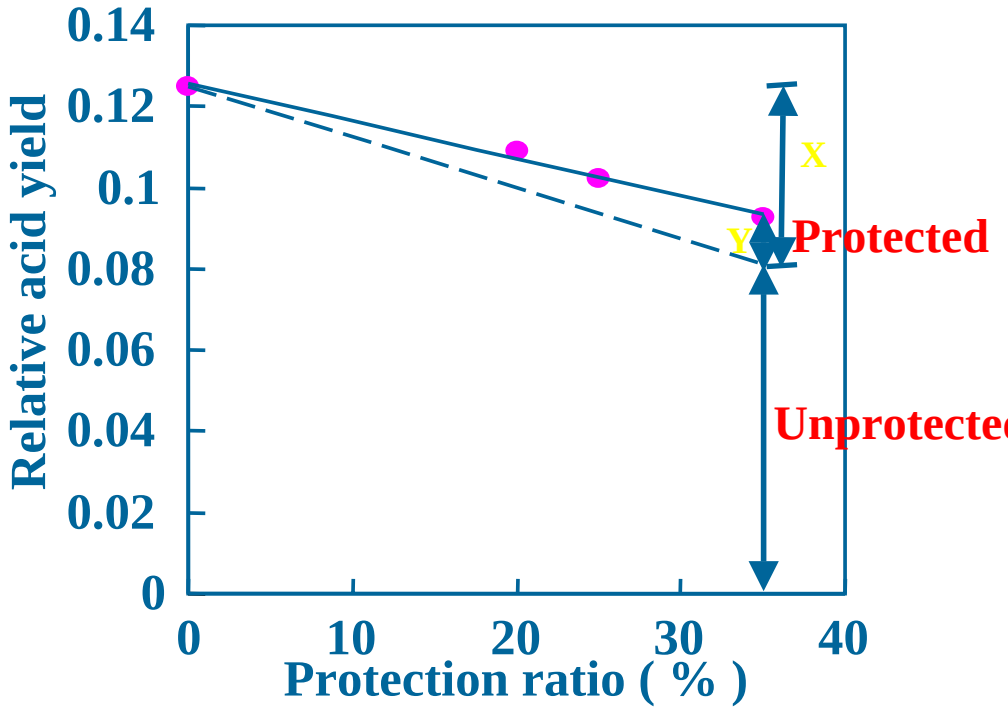


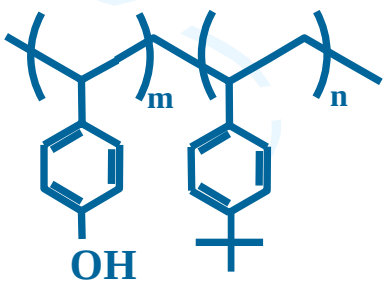


The distribution of probability density of counter anions in the x-y plane. The coordination of ionization point is the origin.

PHS protected with tert-butyl groups



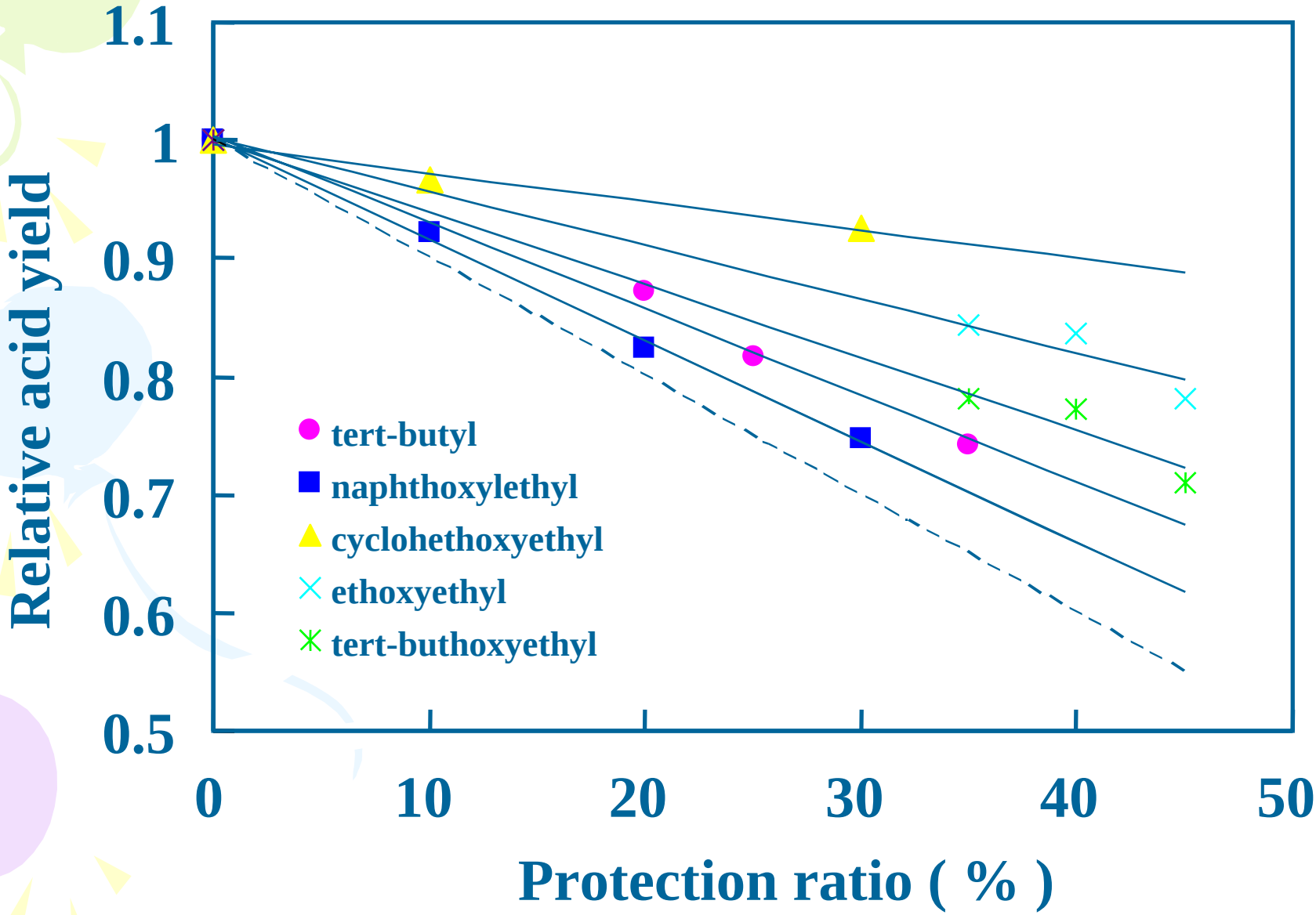




PolymerA

$$\text{Acid generation efficiency} = \frac{Y}{X} \times 100\ (\%)$$

Acid generation efficiency



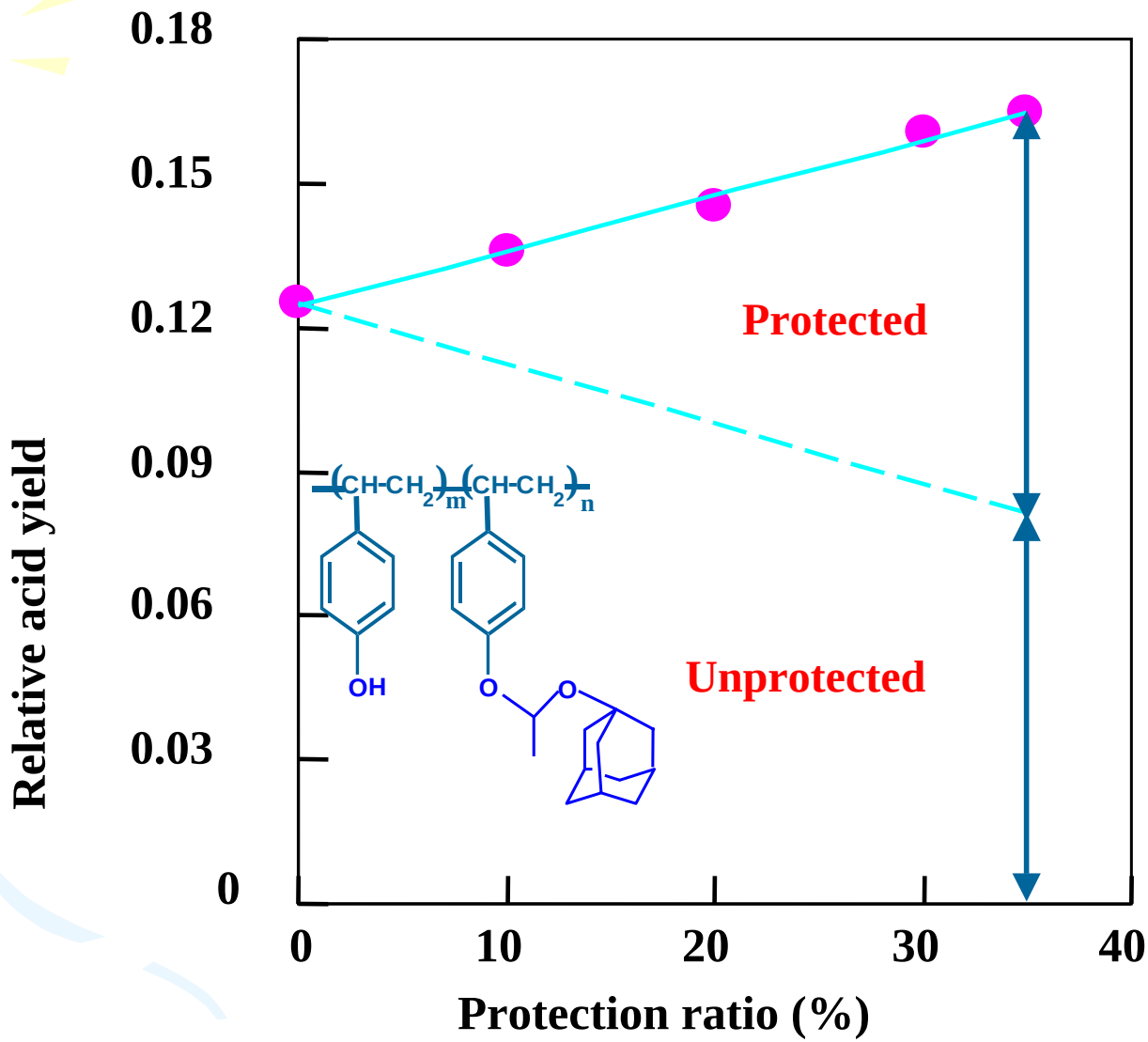
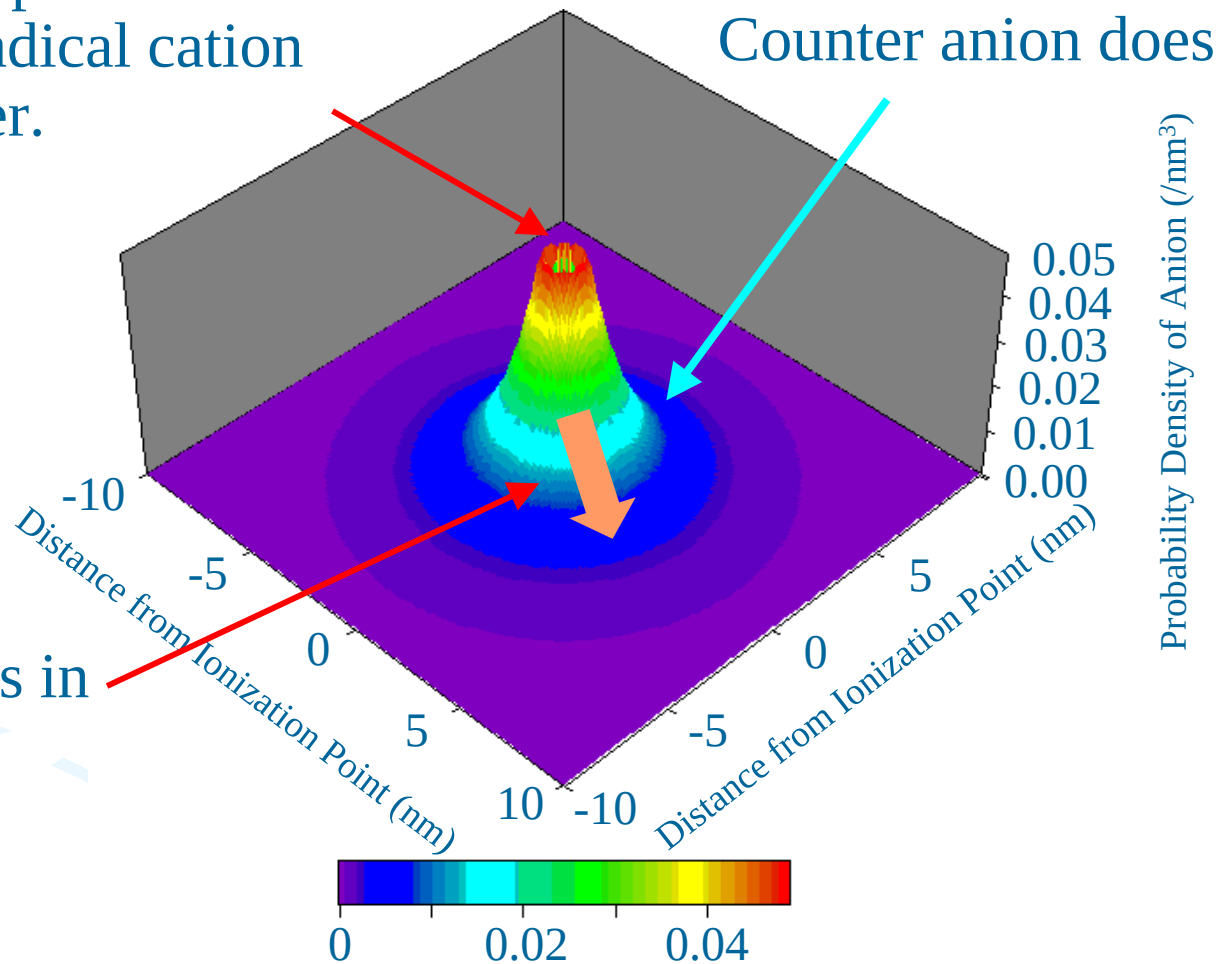


Fig. 4 The relation between relative acid yield and protection ratio of hydroxyl groups by adamantyl groups.

Proton dynamics in chemically amplified resists

Proton is generated here according to deprotonation efficiency of radical cation of base polymer.

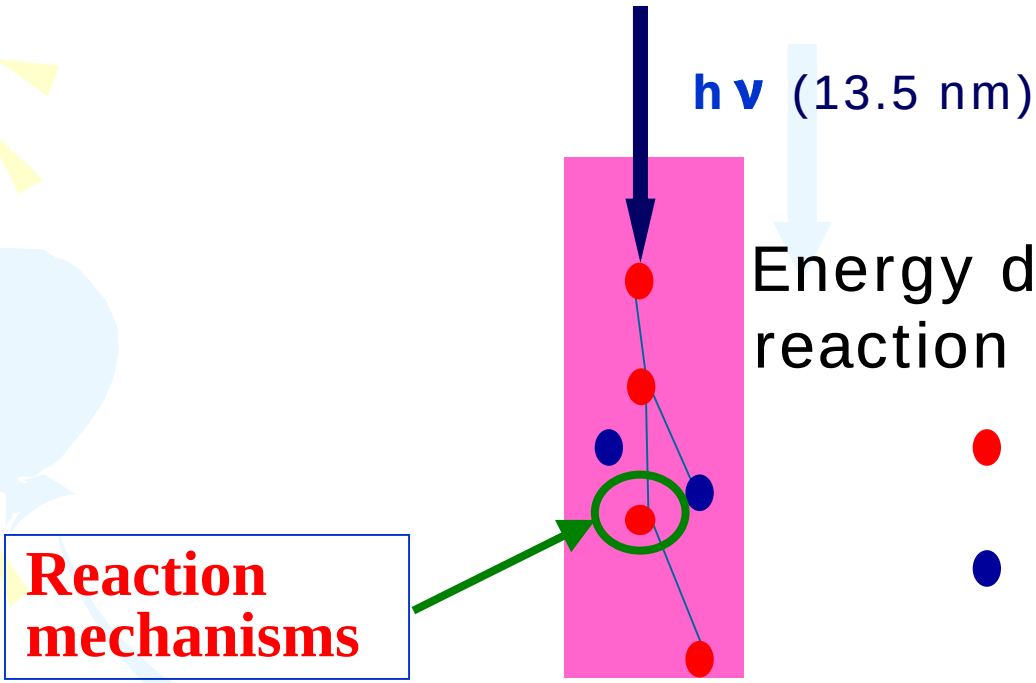
Counter anion does not move.



Proton migrates in resist matrix

Anion distribution ~ **Acid distribution**

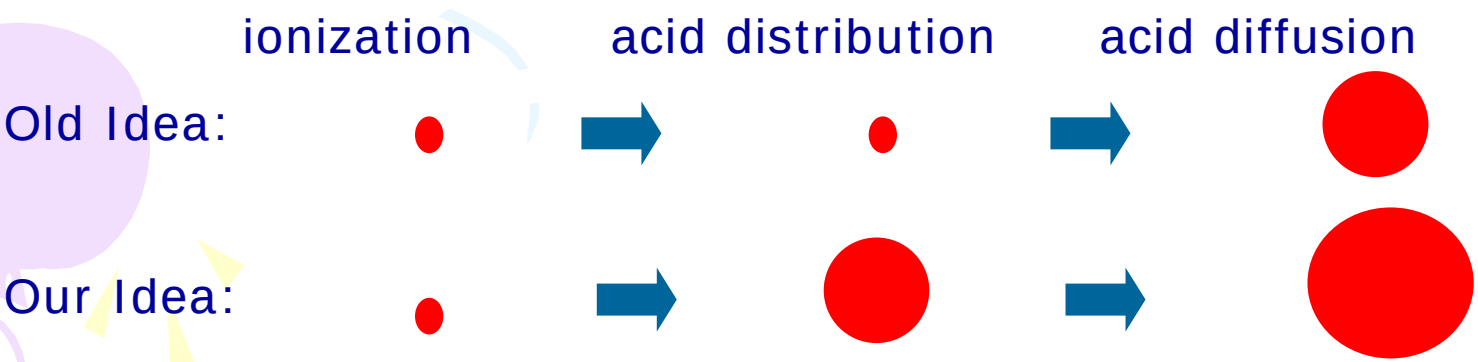
Sensitivity
and
Nanoscale Topology of Resist Patterns



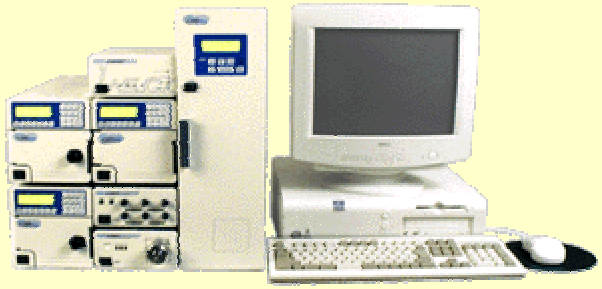
Energy deposition point and reaction point are different.

● **ionization**

● **excitation**



75 and 30 keV EB Exposure Systems and FIB Suystems



Design, Synthesis, and Characterization of Materials

Co-operation

Simulation

Reaction Mechanisms
Pulse Radiolysys System

Resist Research in Tagawa Lab.

Conclusion

1. The energy deposition point and acid formation point are different.
2. The elucidation of the reaction mechanisms of chemically amplified resists is very important in the development of the resists with at least both high sensitivity and high space resolution.
3. Our findings are integrated to a simulation model. This model is applicable to exposure souses whish have higher energy than ionization potential of resist materials. The probability density of acid distribution around ionization point was simulated with a typical parameter set.

Further work should be down for total scheme of EUV resists.