Resist design for 22 nm node

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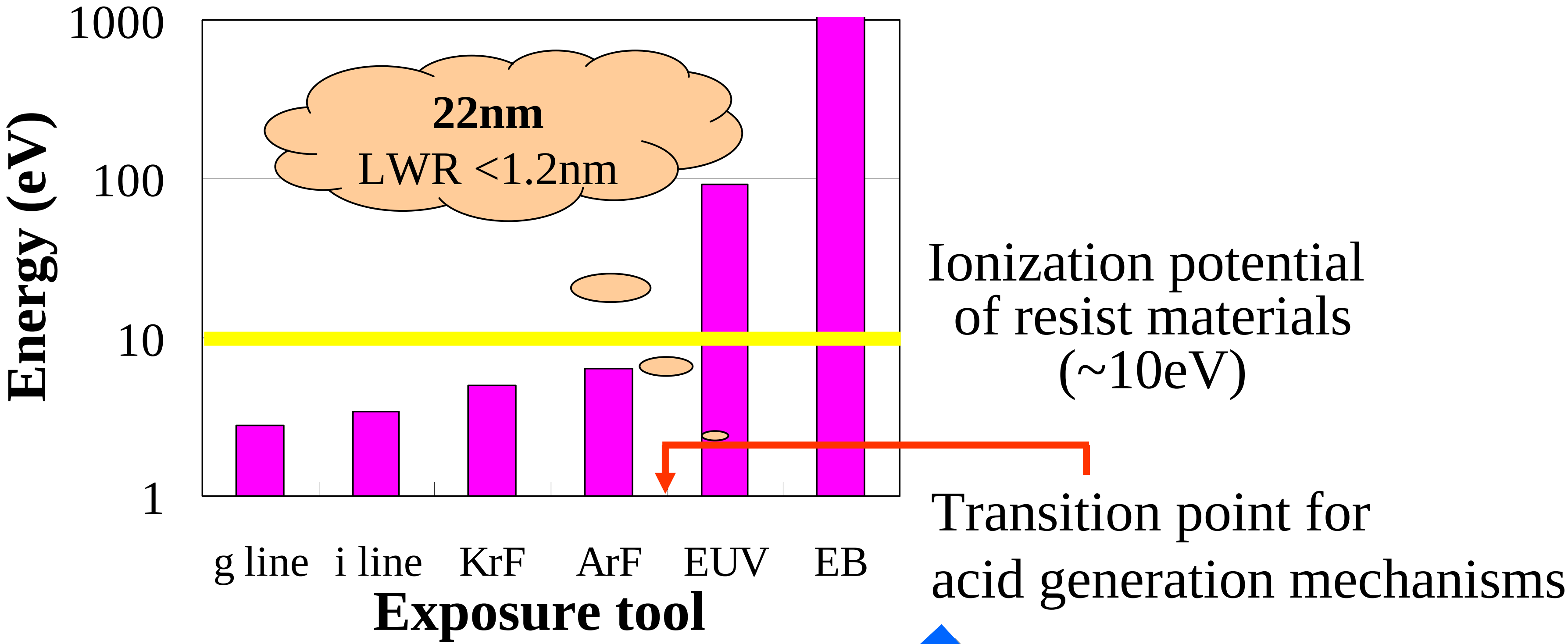
Toward high energy



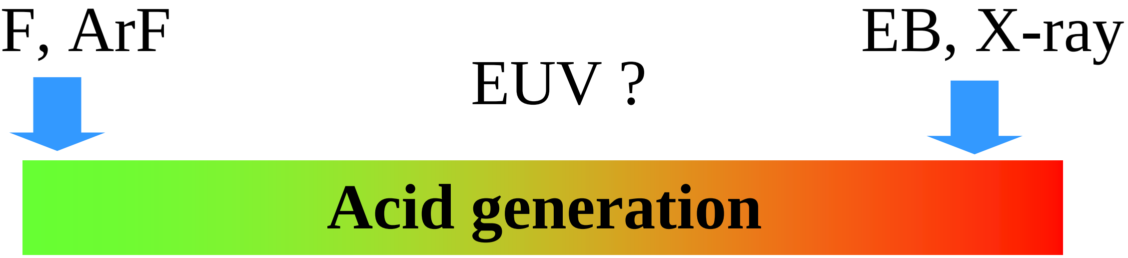
Ionization potential
of resist materials
(~10eV)

Transition point for
acid generation mechanisms

The need for the change of resist design strategy

Acid generation mechanism of EUV resists
Material design for EUV resists

Acid generation mechanism



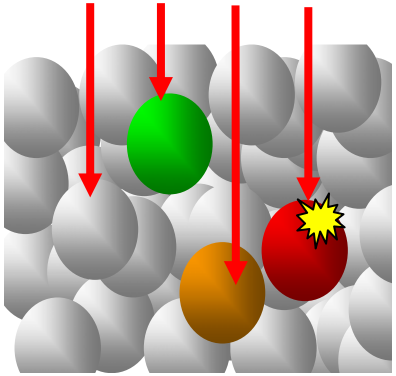
KrF, ArF

EUV ?

EB, X-ray

Acid generation

Excitation path



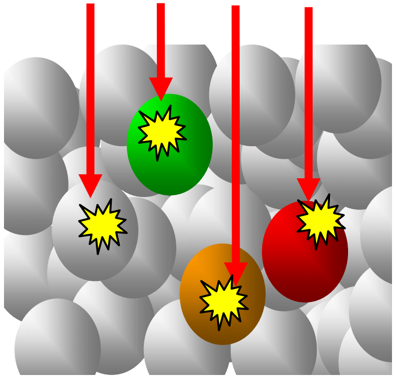
Direct excitation

(In some case, electron transfer from excited polymer)

$$AG \xrightarrow{h\upsilon} AG^*$$

- ⚪ Polymer
- 🔴 Acid generator
- 🟢 Other components
- 🟠 Impurity

Ionization path



Random energy deposition

$$M \xrightarrow{h\upsilon} M^+ + e^-$$ M: Polymer

$$e^- \longrightarrow e^-_{th}$$: thermalization

$$e^-_{th} + AG \longrightarrow A + G^-$$

The difference is critical for resist pattern formation, process simulation and material design.

Resist pattern formation processes

Exposure tool

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

Accumulated energy profile (aerial image)

Conversion of energy to acids

Decomposition of acid generators

Latent acid image

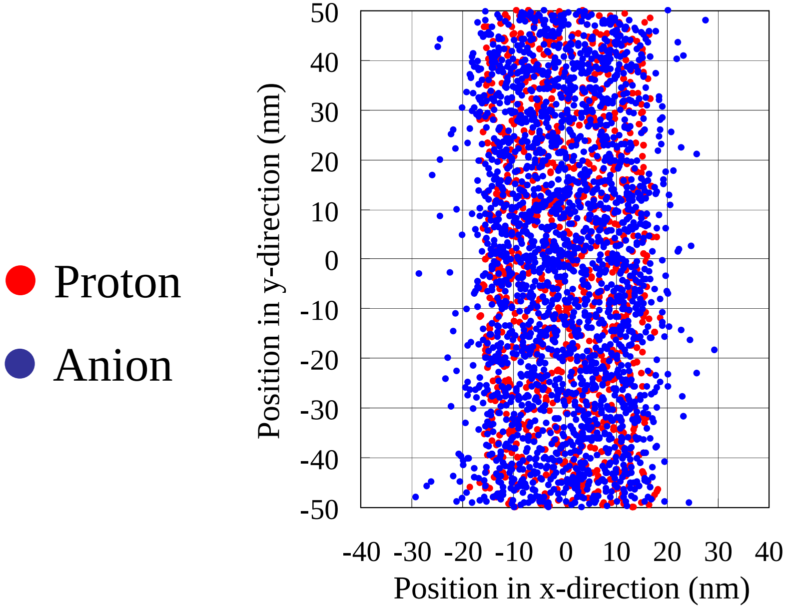
Acid diffusion

Deprotection reaction

Acid catalyzed image (Latent image after PEB)

Development

Different from each other for ionizing radiation



Proton-anion distribution

Significant impact on sensitivity, resolution and LER

T. Kozawa et al., J. Appl. Phys. 99 (2006) 054509.

T. Kozawa et al., J. Vac. Sci. Technol. B23 (2005) 2716.

LER formation mechanism

Initial acid distribution

Aerial image including reflection from substrate and flare
Acid concentration
    Exposure dose — **Process factor**
    Acid generation efficiency — **Material factor**
Shot noise
Specific to EB
    Reaction of acid generator with low energy electron (~0eV)

Catalytic chain reaction (acid diffusion and reaction)

Pre-baking and post-exposure bake conditions (temperature and period) — **Process factor**

Diffusion constant of acid and base quencher
    Glass transition temperature of polymer
    Size of acid counter anion and base quencher
    Residual solvent
Base quencher concentration
Activation energy for catalytic reaction
— **Material factor**

Development and rinse

Development time
Temperature of developer
Strength and molecular size of solvents
Rinse
— **Process factor**

Molecular weight
Molecular dispersion
Rigidity of polymer structure
Polymer aggregation
Crystallization
— **Material factor**

Initial acid distribution

Modification

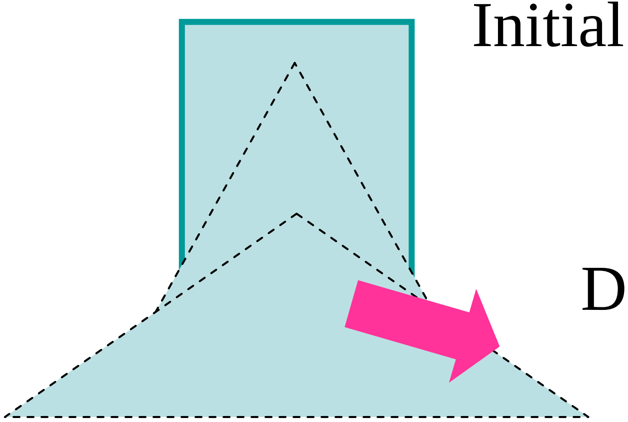
Improved
or
Degraded

LER

Basic strategy for resist development for 22 nm node

Chemical amplification is still needed

- To achieve high sensitivity
- To reduce the statistical effect by acid diffusion



Initial acid distribution

Diffusion

The reduction of catalytic chain length

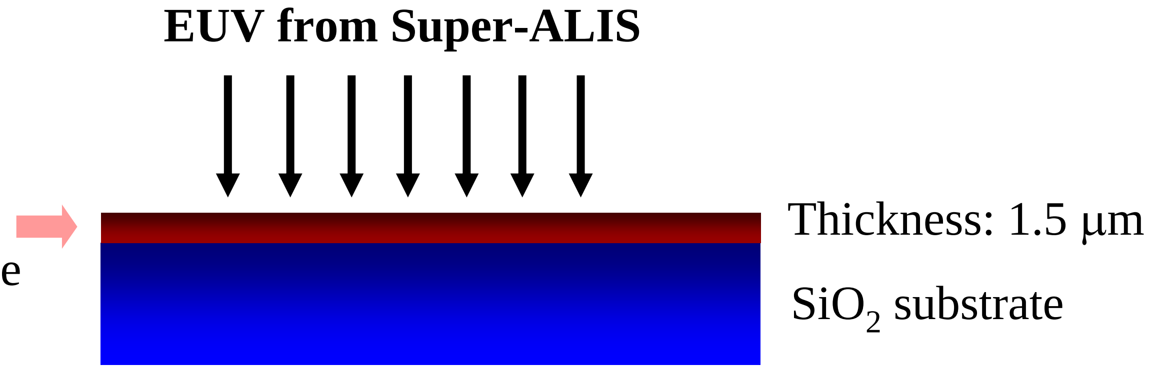
The enhancement of proton production

The improvement of initial image quality of counteranions

Quality of anion distribution and quantity of proton

Experimental

T. Kozawa, H. Oizumi,
I. Nishiyama, S. Tagawa,
JVSTB24(2006)L27.



EUV from Super-ALIS

Poly(4-hydroxystyrene) film with
10 wt% TPS-tf and 5 wt%
Coumarin6 (C6) acid sensitive dye

Thickness: 1.5 μm

SiO_2 substrate

*The exposure dose was evaluated with a diode detector (SXUV100 Mo/Si/SiC, IRD) calibrated at PTB Radiometry Laboratory at BESSY II. The estimated exposure dose (mJ cm^{-2}) per unit beam current (As) was 0.60 ± 0.03 mJ cm^{-2} A^{-1} s^{-1}.

References

Experimental procedure: H. Yamamoto et al., Jpn. J. Appl. Phys., Part 1 43, 3971 (2004).

Flood exposure system: H. Oizumi et al., J. Photopolym. Sci. Technol. 19, 507 (2006).

Acid yield in a model system of chemically amplified EUV resist

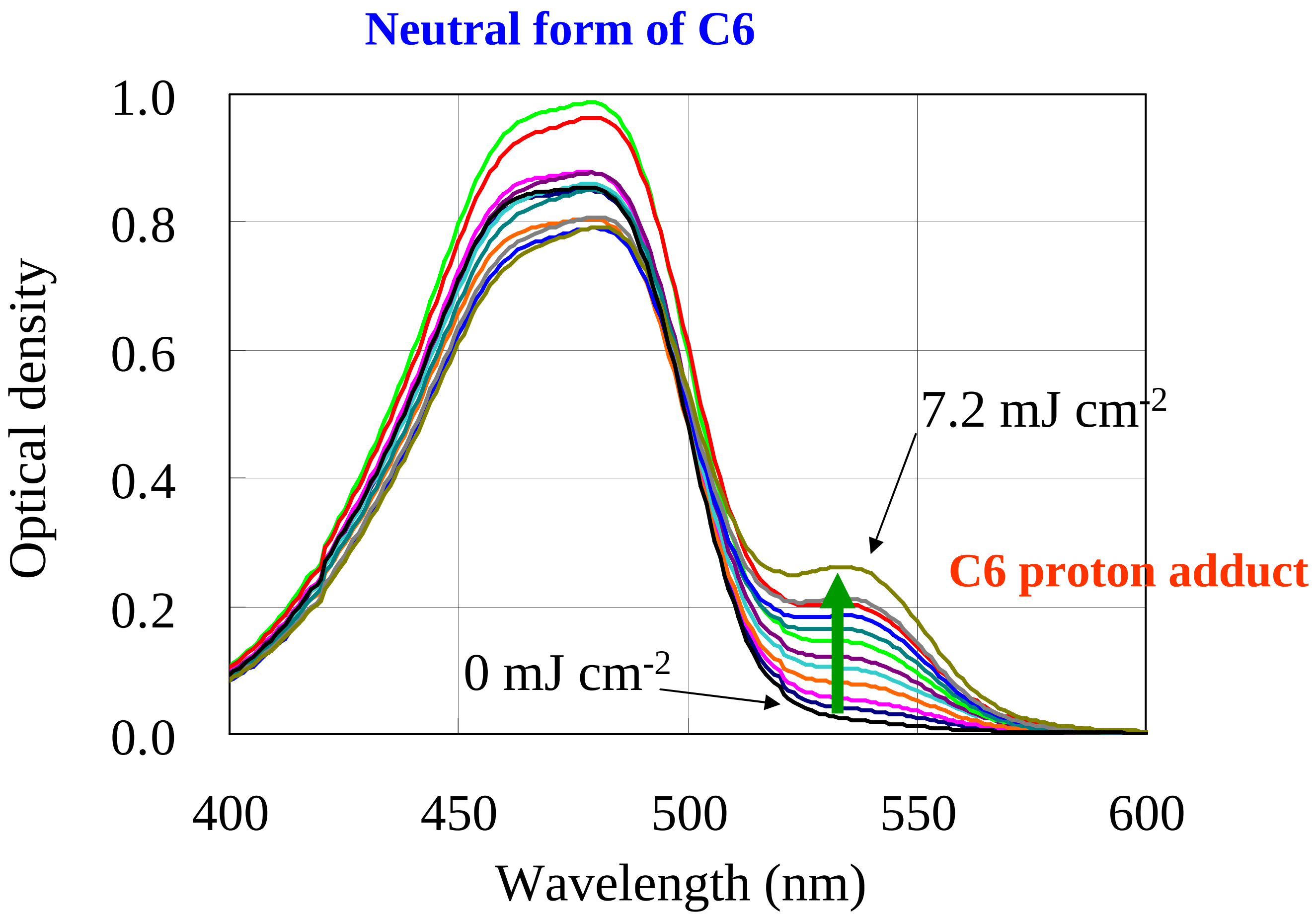
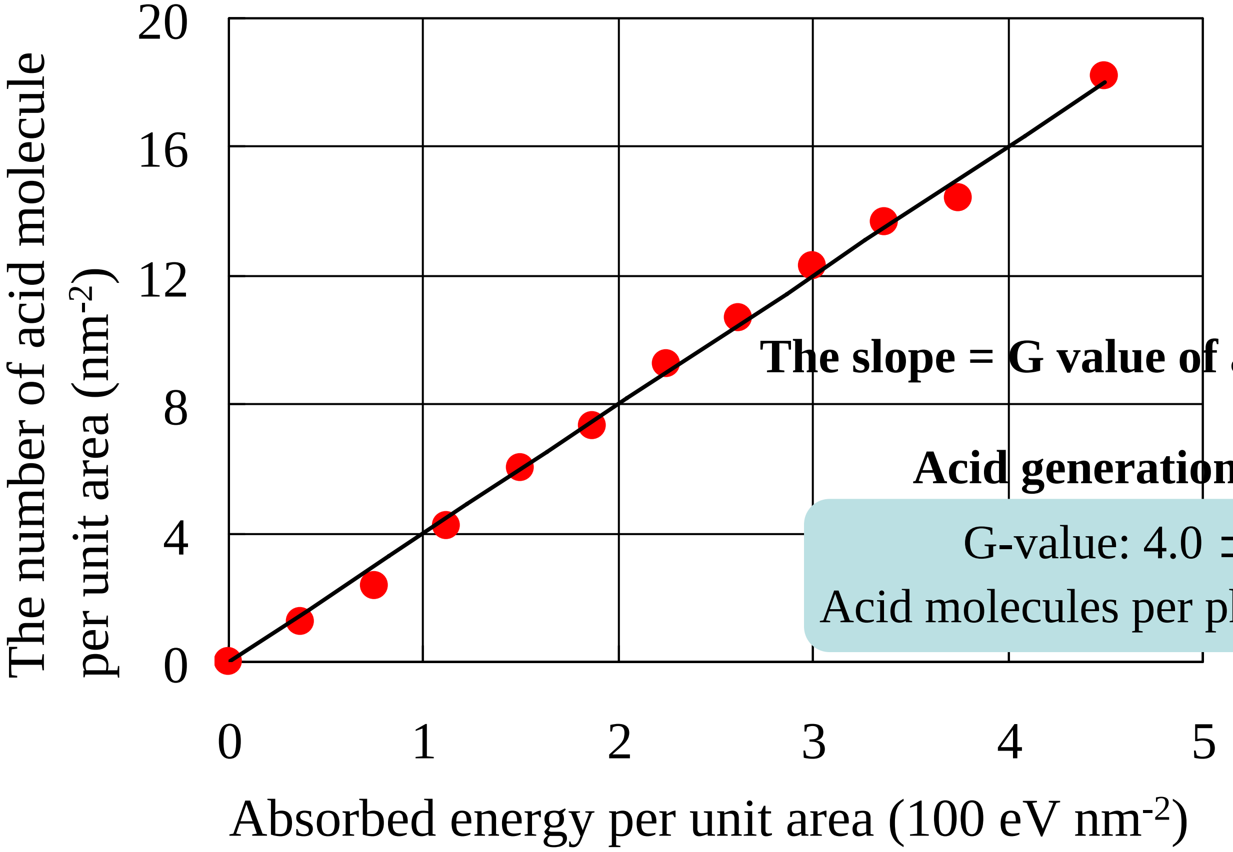


Fig. Absorption spectra of PHS films with 10 wt% TPS-tf and 5 wt% C6 after EUV exposure. The exposure doses are 0, 0.6, 1.2, 1.8, 2.4, 3.0, 3.6, 4.2, 4.8, 5.4, 6.0 and 7.2 mJ cm^{-2} from the bottom to the upper line at the wavelength of 533 nm.

The number of acid molecules generated with 100 eV absorbed energy (G-value)



The slope = G value of acid generation

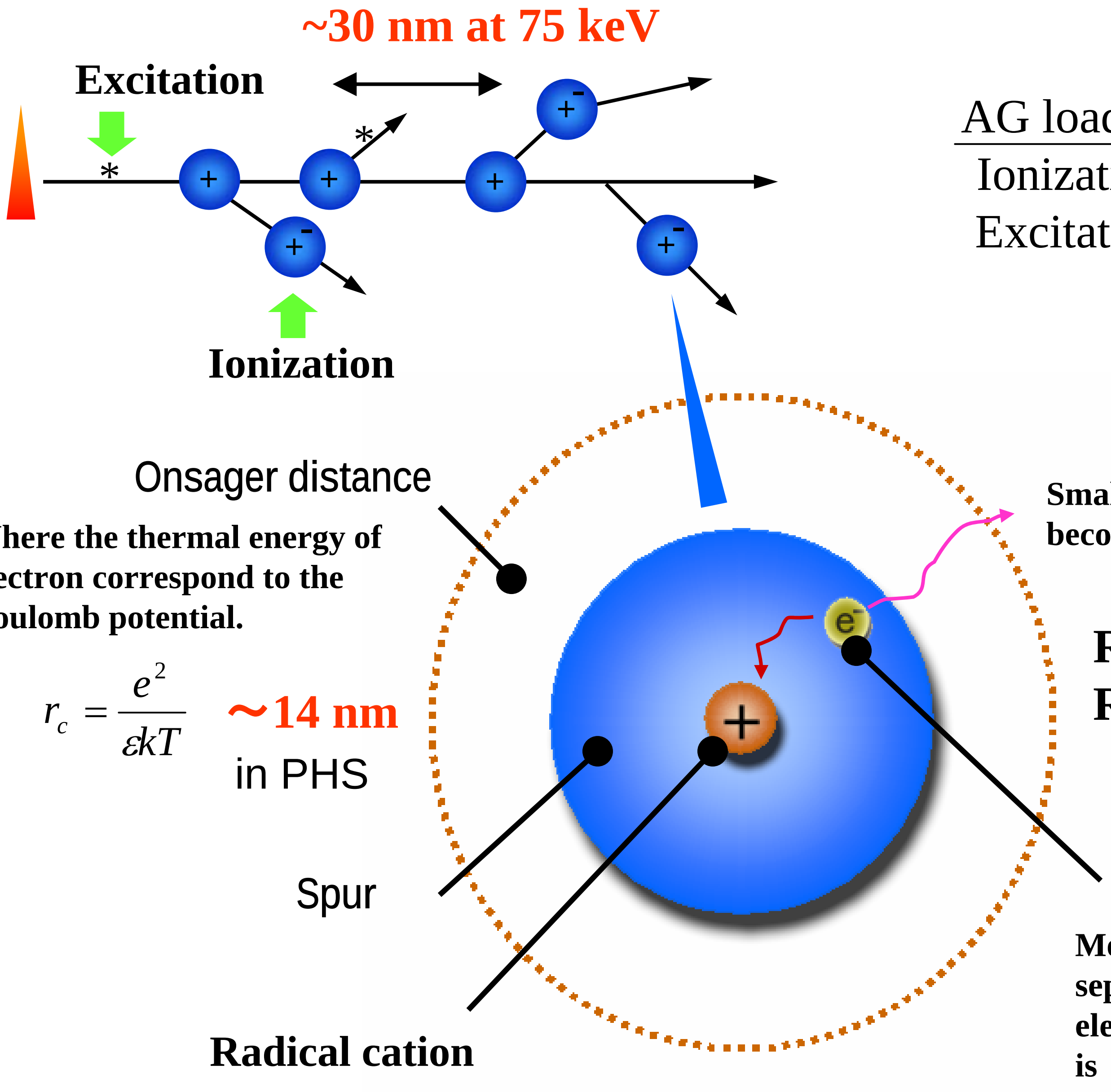
Acid generation efficiency

G-value: 4.0 ± 0.2

Acid molecules per photon: 3.7 ± 0.2

Fig. Relation between the absorbed energy per unit area and the number of acid molecules generated by EUV exposure per unit area.

Interaction of electron with material -spatial distribution-



Where the thermal energy of electron correspond to the Coulomb potential.

$$r_c = \frac{e^2}{\varepsilon kT}$$

~14 nm in PHS

AG loading	5 wt%	10 wt%
Ionization	93	90
Excitation	7	10

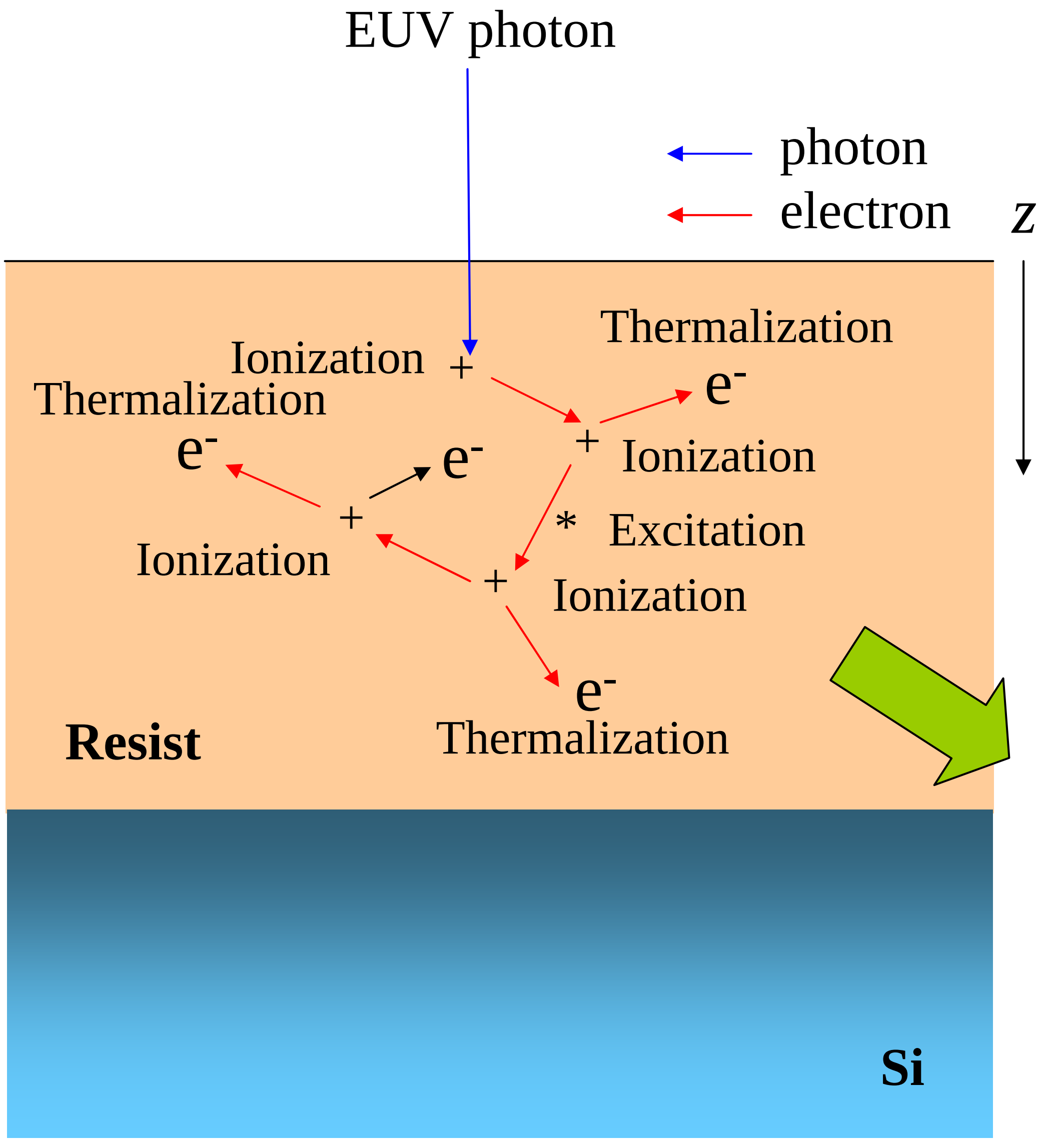
Small part of electrons become free.

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

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

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

Interaction of EUV photon with material -spatial distribution-



Intensity of EUV (I)

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

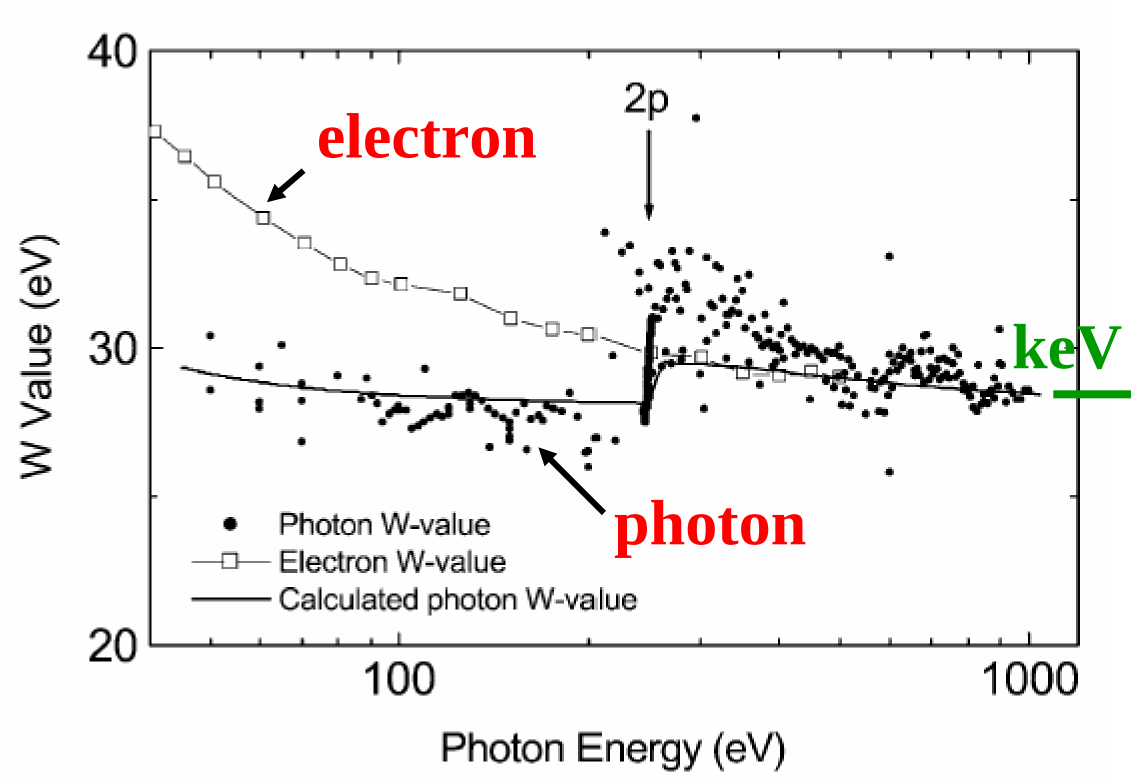
Absorption coefficient (α)

PHS : 3.8 μm^{-1}

The number of secondary electrons can be estimated using W-value.

Average energy required to produce an ion pair (W-value)

How many secondary electrons are generated?



$$\text{W-value} = \frac{100\ (\text{eV})}{\text{G-value}}$$

Ionization energy (Ar):
15.759, 15.937 eV

Insensitive to quality and energy for radiations above keV

K-edge

Carbon: 284 eV

Oxygen: 547 eV

Fig. 3. Photon W-value for Ar as a function of photon energy. The solid circles show the present result, and the open squares are the data of Combecher for electrons. The solid curve represents the photon W-values calculated by the model here. The arrow indicates the 2p ionization threshold. [N. Saito, I. H. Suzuki, Radiat. Phys. Chem. 60 (2001) 291.]

W-value in PHS

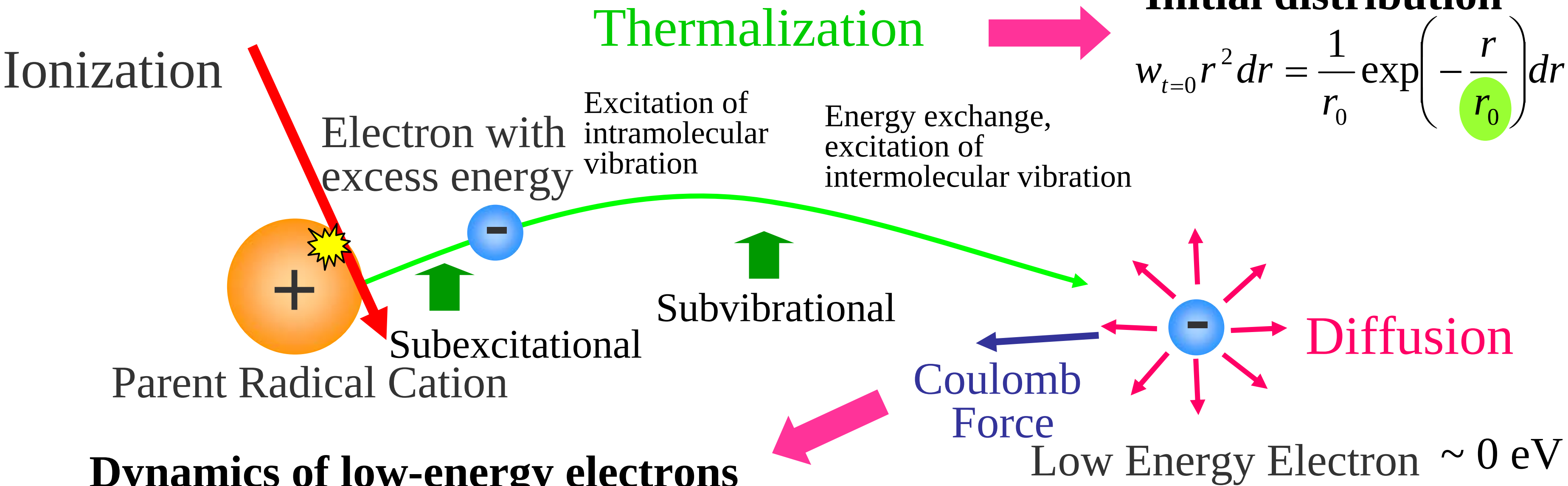
22.2 eV (75 keV EB)

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

92.5/22.2 = **4.2**

Generation efficiency of counteranion per ionization

Decomposition of acid generator through the reaction with low-energy electron



Ionization

Electron with excess energy

Excitation of intramolecular vibration

Thermalization

Energy exchange, excitation of intermolecular vibration

Subexcitational

Subvibrational

Parent Radical Cation

Initial distribution

$$w_{t=0} r^2 dr = \frac{1}{r_0}\exp\left(-\frac{r}{r_0}\right)dr$$

Diffusion

Coulomb Force

Low Energy Electron ~ 0 eV

Acid generator react with these low energy electrons.

Dynamics of low-energy electrons

Coulomb interaction

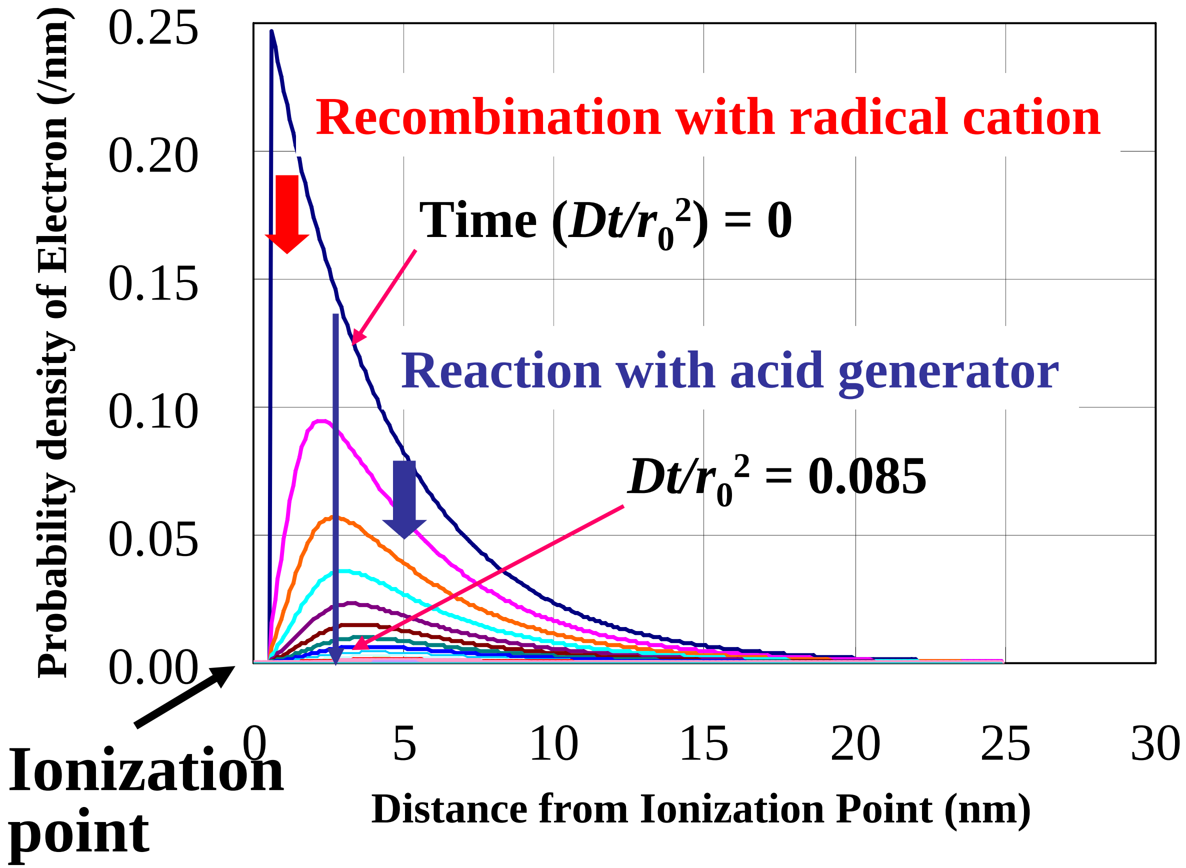
$$\frac{\partial w}{\partial D_e t} = \nabla\left(\nabla w + w\frac{1}{k_B T}\nabla V\right) - 4\pi R_{AG} C_{AG} w$$

Diffusion

Reaction with acid generator

Generation efficiency of counteranion per ionization : $$\phi_{AG(electron)} = \frac{4\pi\int_0^\infty\int_{r_+}^\infty R_{AG} C_{AG} w r^2 dr\, d(D_e t)}{\int_{r_+}^\infty w_{t=0} r^2 dr}$$

Electron dynamics in chemically amplified resists



Concentration of AG

C_{AG} = 10 wt%

Initial separation distance

r_0 = 4 nm

Dielectric constant

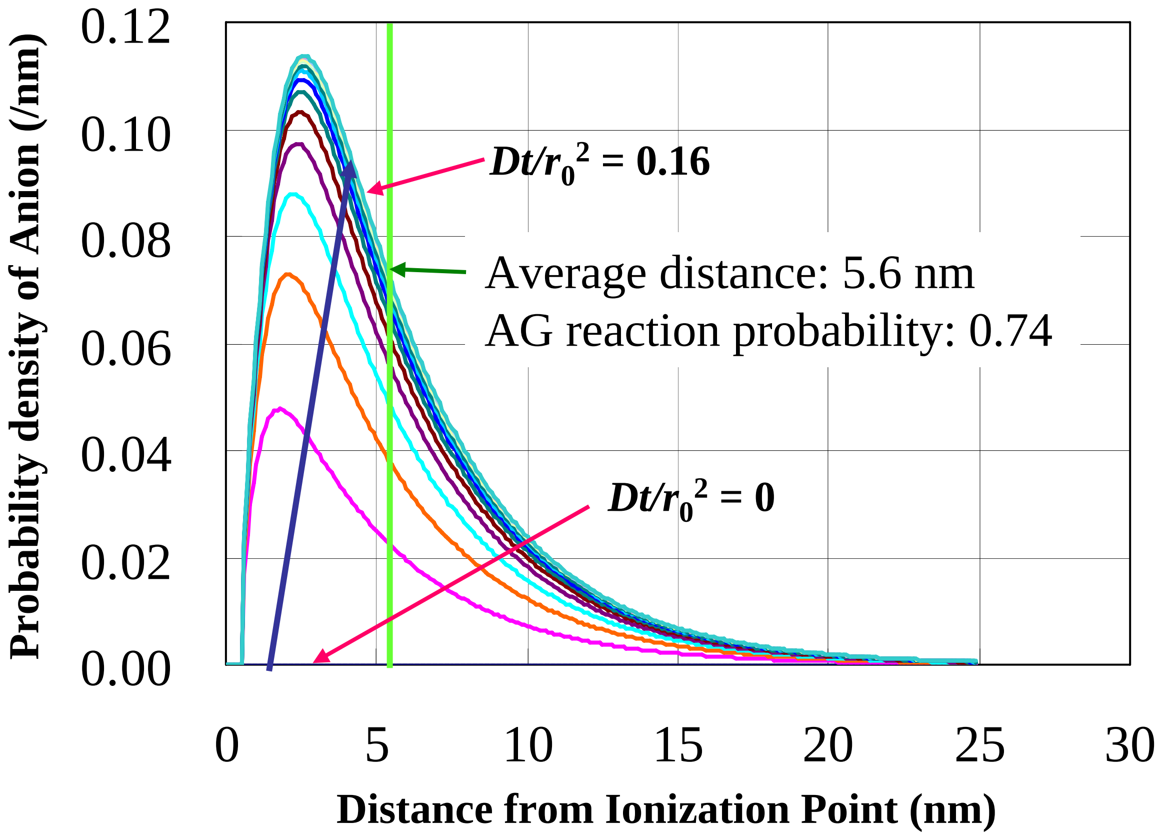
ε = 4

Effective reaction radius

R_{AG} = 2.4 nm

Fig. The distribution change of electrons calculated with the parameters: the concentration of acid generator, C = 10 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 0.085.

Generation probability and distribution of counter anion

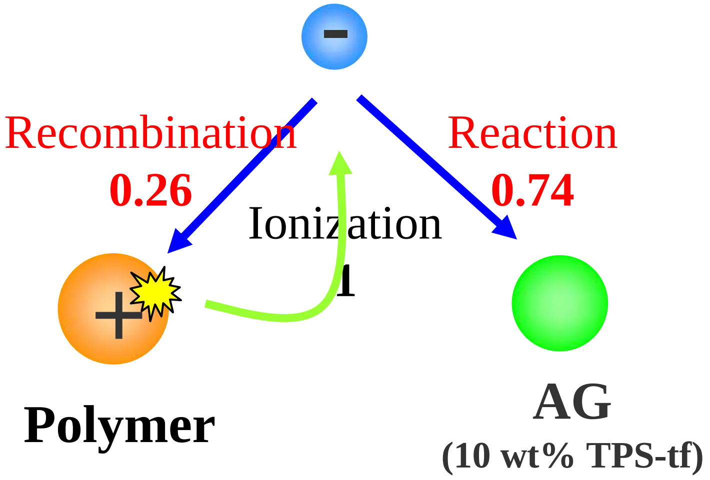


$Dt/r_0^2 = 0.16$

Average distance: 5.6 nm

AG reaction probability: 0.74

$Dt/r_0^2 = 0$



Recombination **0.26**

Reaction **0.74**

Ionization

1

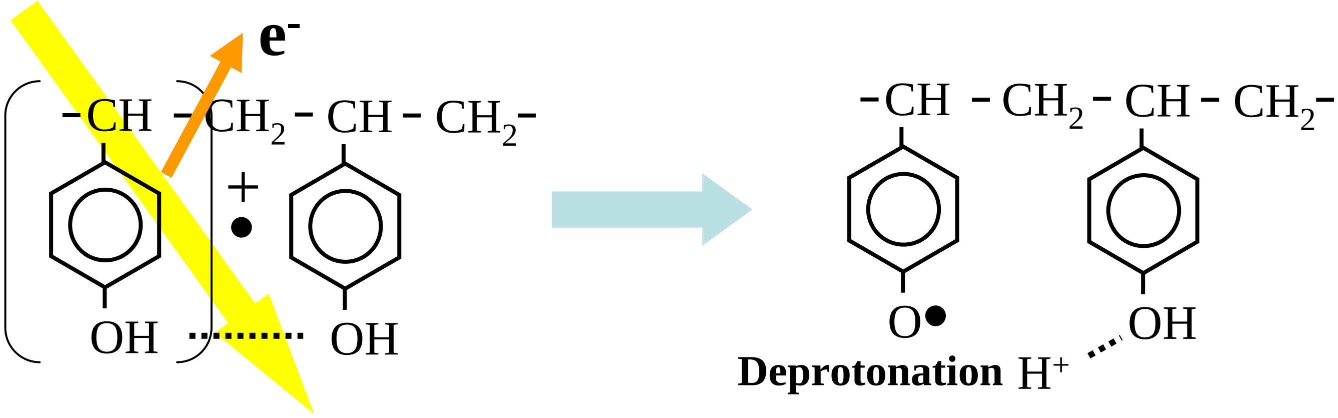
Polymer

AG

(10 wt% TPS-tf)

Fig. The evolution of counter anion distribution calculated with the parameters: the concentration of acid generator, C = 10 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 0.085.

Acid generation efficiency (ionization path)



Ionization

Proton generation

Acid generation probability per ionization

$$\phi_{acid\,(ionization)} = \phi_{polymer+}\phi_{AG\,(electron)}$$

Deprotonation efficiency of polymer radical cation

Acid yield per 100 eV absorbed energy (ionization path)

$$G_{acid\,(ionization)} = \phi_{acid\,(ionization)} G_{ionization}$$

The number of acid molecule per 100 eV

The number of ionization per 100 eV

Predicted acid generation efficiency in PHS

$$G_{ionization}(PHS) = \frac{100}{W_{PHS}} = \frac{100}{22.2} = 4.5$$

$$\phi_{polymer+}(PHS) = 1$$

$$G_{acid\,(ionization)} = 1 \times 0.74 \times 4.5 = 3.3$$

per photon

3.3 x 0.925 = 3.1 (3.7)

Acid generation through direct excitation and polymer sensitization

Dill's formulation (direct excitation)

$$\frac{\partial I(x,t)}{\partial x} = -I(x,t)\left[A_{Dill} M(x,t) + B_{Dill}\right]$$

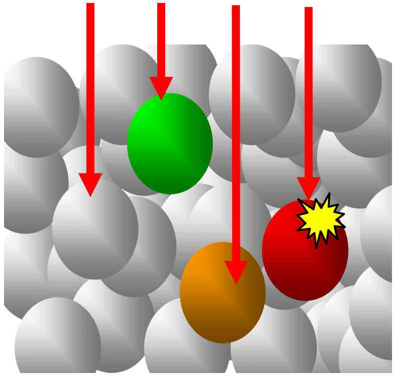
$$\frac{\partial M(x,t)}{\partial t} = -I(x,t) M(x,t) C_{Dill}$$

I : Light intensity

M : Fractional inhibitor concentration

A_{Dill}, B_{Dill}, C_{Dill} : Constants

Excitation path



Excitation
and
Polymer sensitization

Polymer sensitization (energy or electron transfer from excited state of polymer)

Static quenching (Perrin model)

$$\ln\left(I_{f0} / I_f\right) = V_f N C_{AG}$$

Acid yield per 100 eV absorbed energy (excitation path)

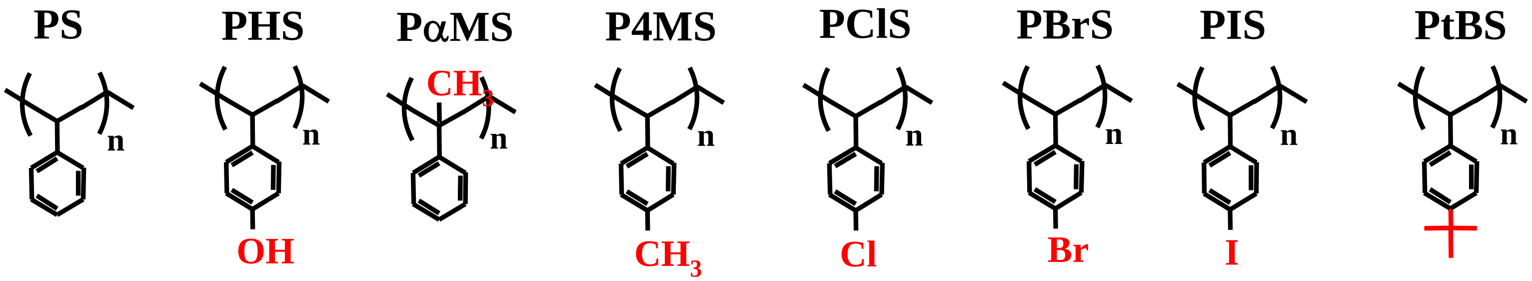
$$G_{acid\,(excitation)} = f_{excitation} C_{AG}$$

AG loading	5 wt%	10 wt%
Ionization	93	90
Excitation	7	10

Polymer structure dependence of acid yield

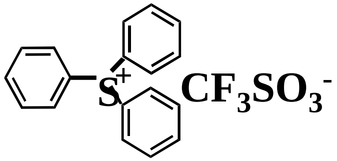
JJAP46(2007)L142

Polymer



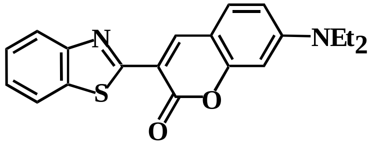
Acid generator

TPS-tf



Acid sensitive dye

Coumarin 6



Relative acid yield

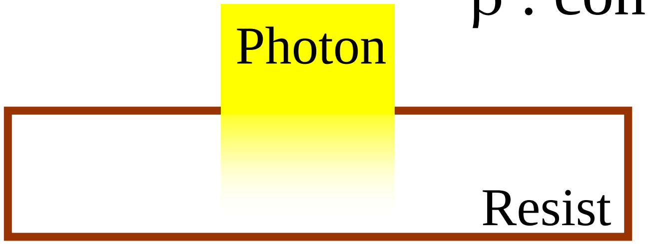
	EUV (%)	EB (%)
PHS	100.0	100.0
PBrS	40.4	45.4
PClS	29.5	38.2
PIS	14.2	
P4MS	7.9	12.6
PαMS	2.0	7.1
PtBS	6.5	
PS	5.3	5.5

PHS vs. PS, P4MS

$$\frac{\partial I}{\partial z} = -\left(\alpha_{polym}\beta_{polym} + \alpha_{AG}\beta_{AG}\right)I$$

α : absorption coefficient

β : concentration (component ratio)



When all the photons are absorbed by resist film….

	α_{polym}	Relative absorption by acid generator	Total acid yield
KrF, ArF	High	Low	Low
	Low	High	High
EUV	PHS 3.80 /μm	Low	100.0
	PS 2.79 /μm	High	5.5
	P4MS 2.66 /μm		12.6

Resist design of EUV resists (1)

For the resist design, the most critical point is which molecule absorbs incident radiation.

Photoresist

The basic design strategy of photoresists is to minimize the absorption of polymer and adjust that of acid generator to an appropriate value.

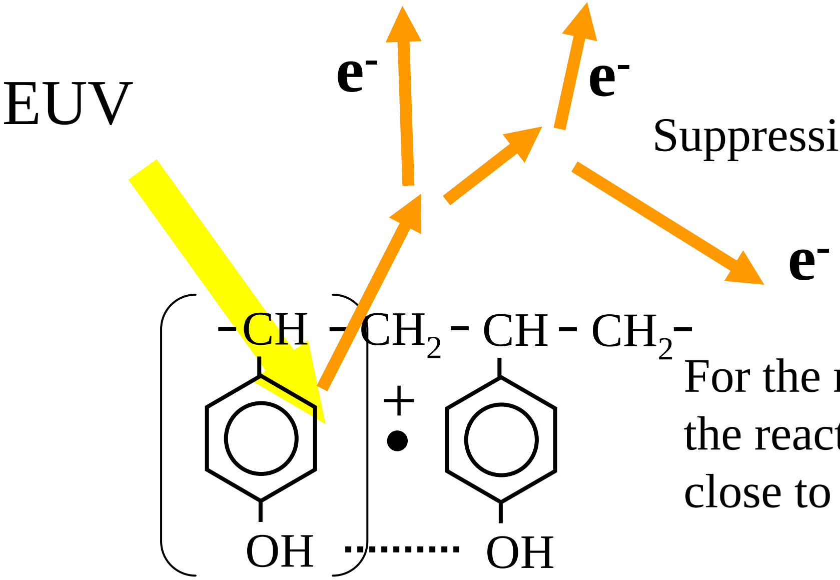
Tremendous efforts have been devoted to the reduction of polymer absorption during the development of KrF, ArF and F_2 excimer laser lithography without exception.

EUV resist

Acid generators are sensitized mainly by not the incident radiation but secondary electrons.

The absorption coefficient of polymers against EUV is more important for acid generation than that of acid generators. The absorption coefficient of polymers should be adjusted to an appropriate value.

Resist design of EUV resists (2)



The number of
secondary electrons

Suppression of electron loss channel

For the reaction with thermalized electron,
the reactivity of current acid generator is
close to physical limit.

Deprotonation efficiency

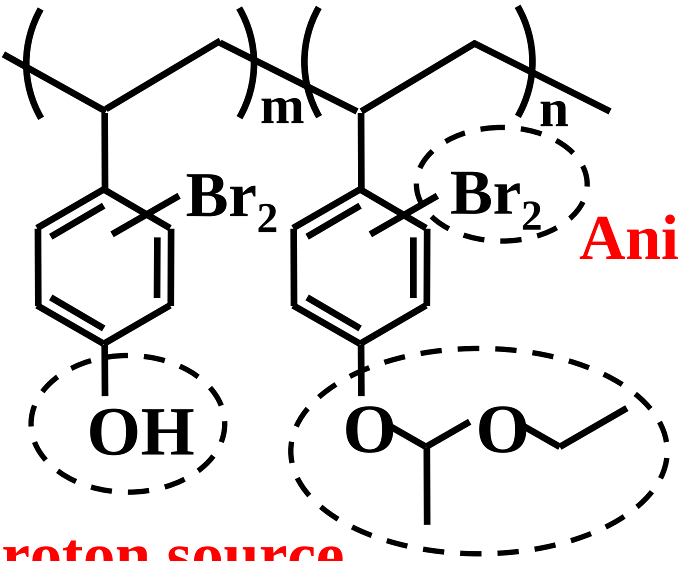
(Acidity of polymer radical cation)

Polymers play an important role in acid generation in EUV resists.

Because of high energy of EUV photon, any polymers and compounds are candidate.

New Chemistry

SPIE[6519-98]



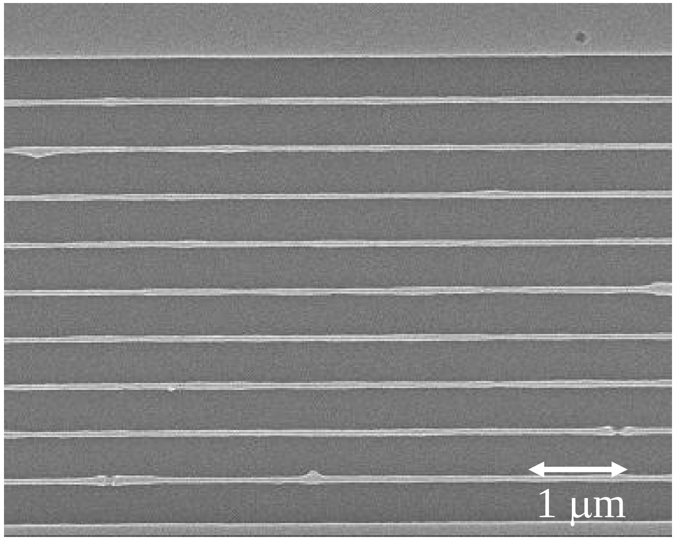
Anion source

Proton source

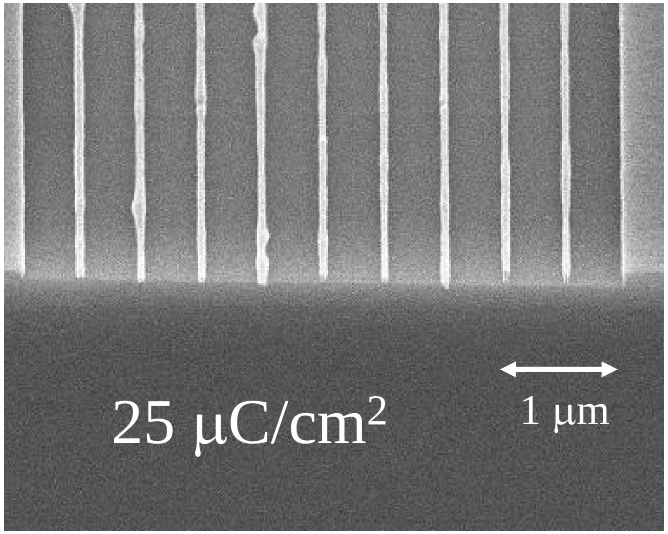
Polarity change

Single component resist
for ionizing radiation

without base quencher
without acid generator



(a) Top-down view



(b) Cross-sectional view

Take advantage of high energy!