Sensitization mechanisms of chemically amplified EUV resists and resist design for 22 nm node

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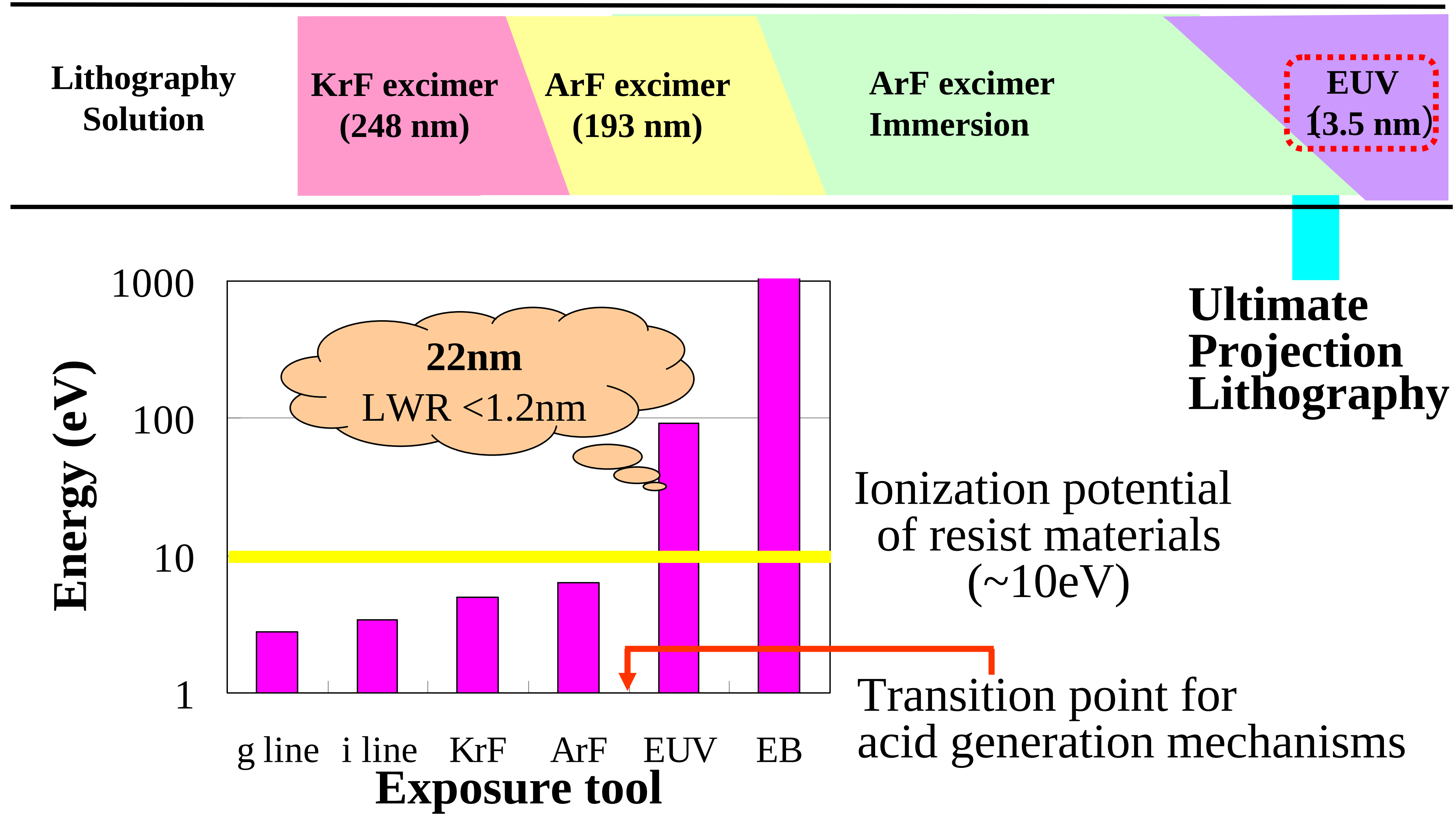
Lithography Roadmap

Year	2001	02	03	04	05	06	07	08	09	10	11	12	13	14	15	16
Technology Node	130			90			65			45			32			22
LWR (nm)							3.4			2.4			1.7			1.2

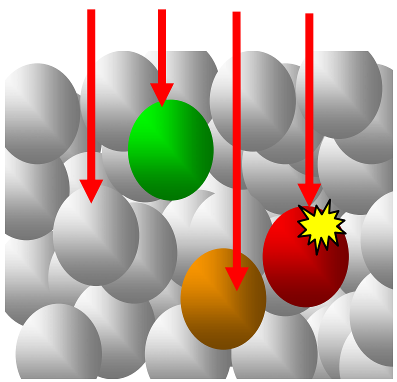


Acid generation processes

KrF, ArF | EB, EUV

Acid generation

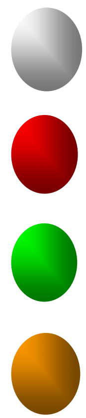
Excitation path



Direct excitation

(In some case, electron transfer from excited polymer)

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



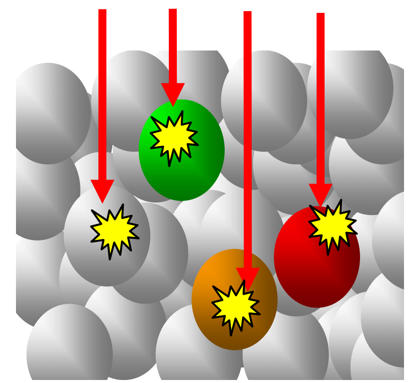
Polymer

Acid generator

Other components

Impurity

Ionization path



Random energy deposition

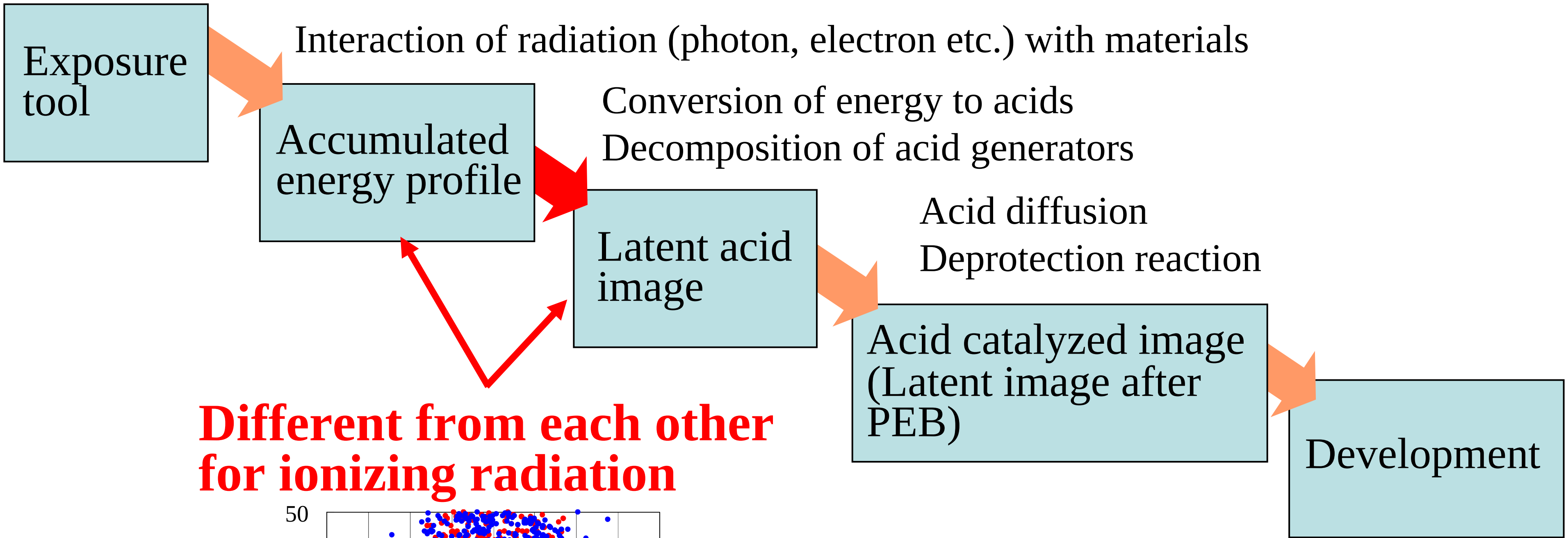
$$M \xrightarrow{h\upsilon} M^+ + e^- \quad \text{M: Polymer}$$

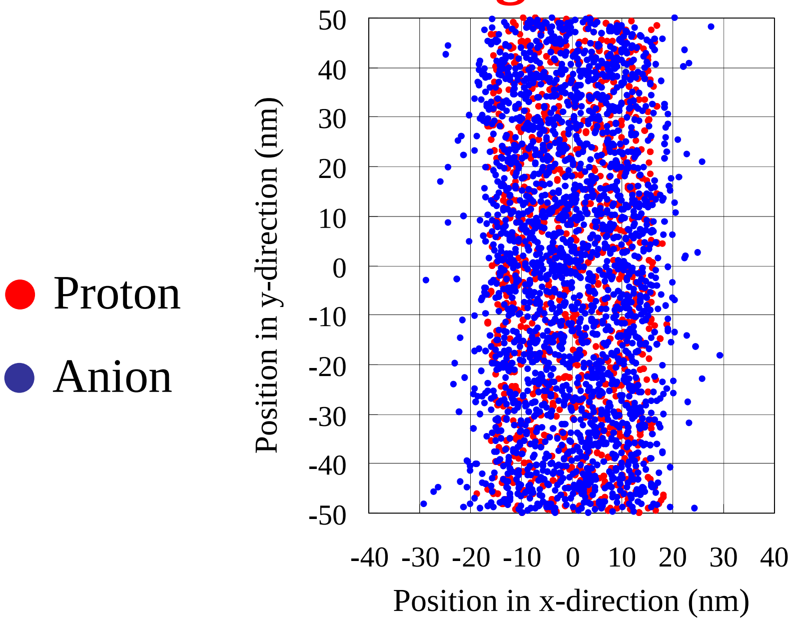
$$e^- \longrightarrow e^-_{th} \quad \text{: thermalization}$$

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

T. Kozawa et al., Jpn. J. Appl. Phys. 31 (1992) 4301.

Resist pattern formation processes





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.

Fundamental research on acid generation is strongly needed.

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 and EUV
- *Reaction of acid generator with low energy electron (~0eV)*

Catalytic chain reaction (acid diffusion and reaction)

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

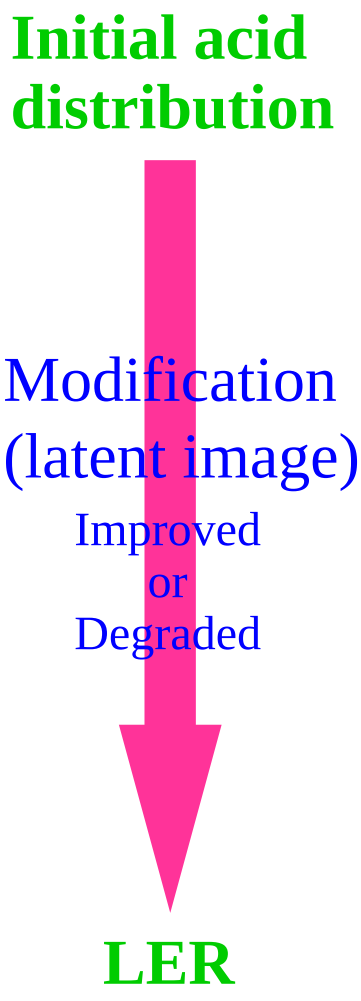
Material factor:
Diffusion constant of acid and base quencher
- Glass transition temperature of polymer
- Size of acid counter anion and base quencher
- Residual solvent

Base quencher concentration
Activation energy for catalytic reaction and diffusion

Development and rinse

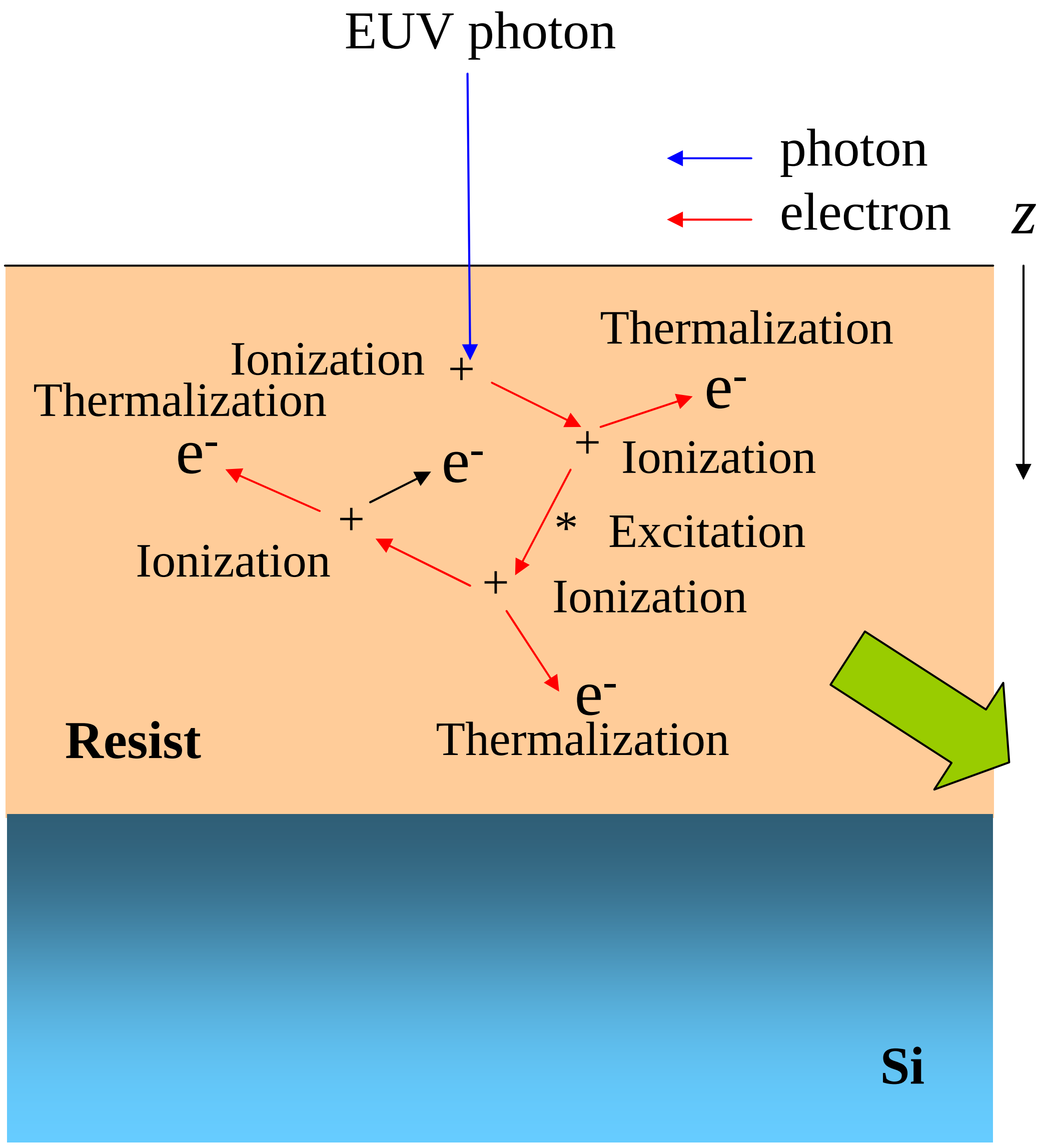
Process factor:
Development time
Temperature of developer
Strength and molecular size of solvents
Rinse

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



T. Kozawa et al., J. Vac. Sci. Technol. B 25 (2007) 2295.

Interaction of EUV photon with material -spatial distribution-



Intensity of EUV (I)

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

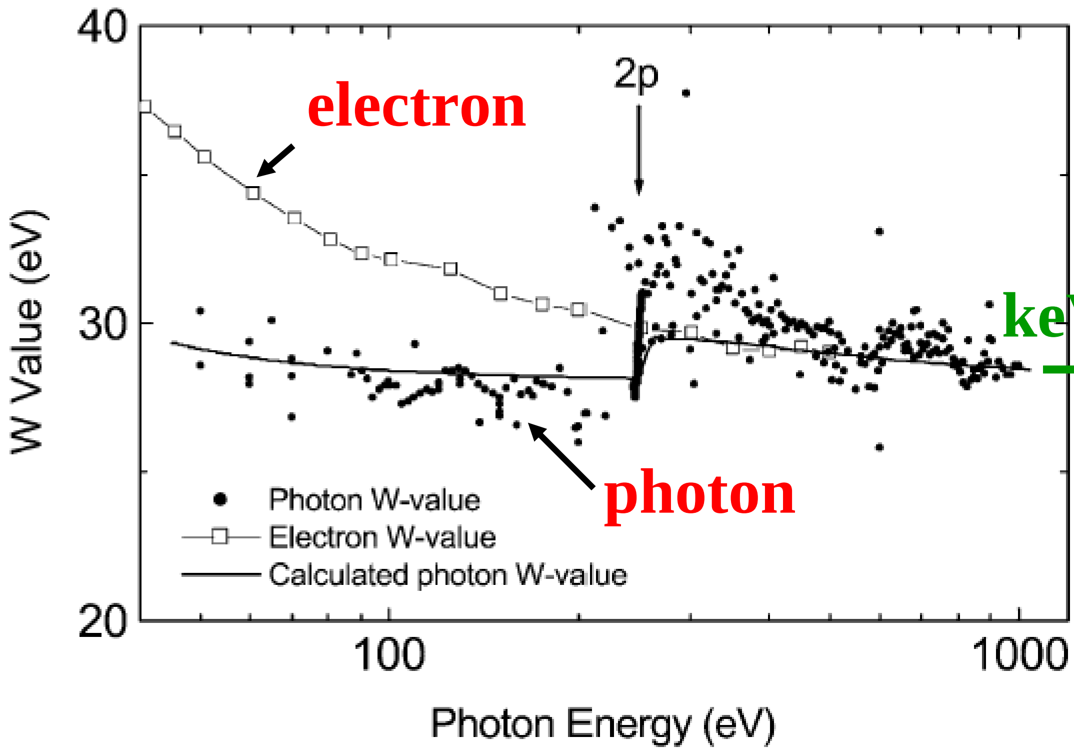
Absorption coefficient (α)

PHS : 3.8 μm^{-1}

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

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

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



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

keV — MeV

Insensitive to quality and energy for radiations above keV

K-edge

Carbon: 284 eV

Oxygen: 547 eV

Fig. 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, 291 (2001).]

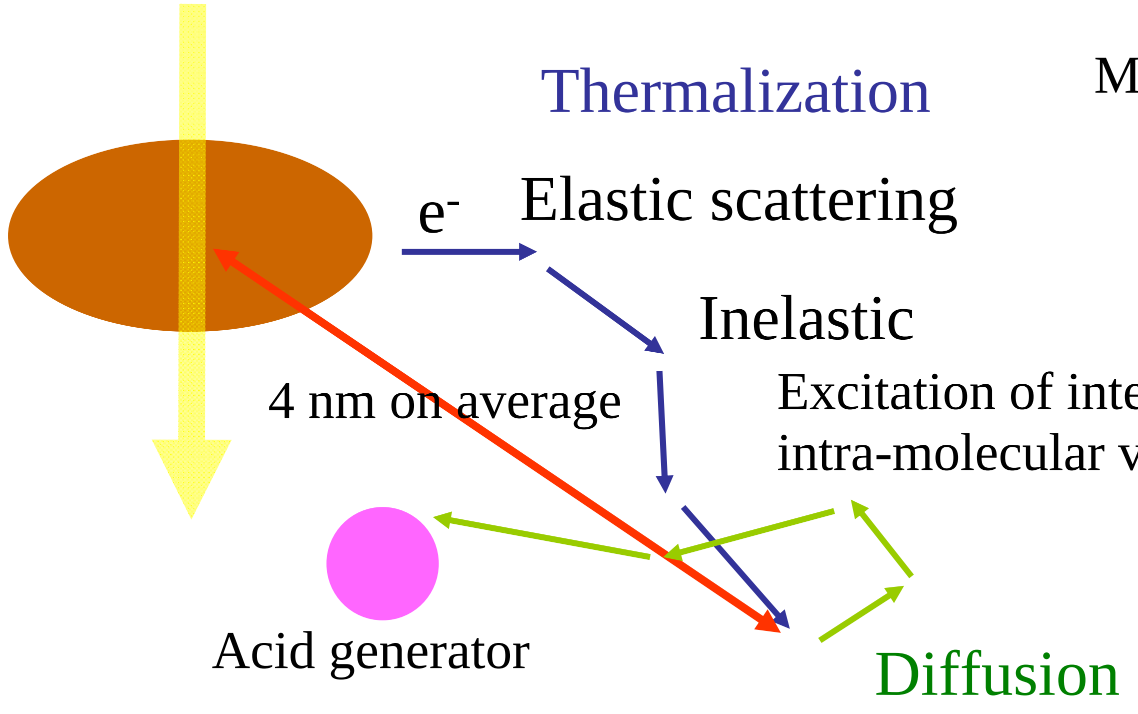
W-value in PHS

22.2 eV (75 keV EB)

[JVST B24, 3055(2006)]

Average number of secondary electrons per EUV photon = 92.5/22.2 = **4.2**

Angular distribution



Mean free path

$$\frac{1}{\lambda} = \frac{1}{\lambda_{inelastic}} + \frac{1}{\lambda_{elastic}}$$

$$\lambda_{inelastic} \geq \lambda_{elastic}$$

Ineffective

Directionality is largely lost during thermalization and subsequent diffusion.

$$p_{AG(electron)}(R) = \frac{\int_0^{\infty} R_{AG} C_{AG} wd(D_e t)}{\int_{r_+}^{\infty} w_{t=0} r^2 dr}$$

Anion probability density around ionization point

Uniform angular distribution

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

T. Kozawa et al., J. Vac. Sci. Technol. B 25 (2007) 2295.

Acid generation efficiency $\phi_{acid\,(ionization)}$

Definition : Acid generation probability per ionization

Proton generation

Protons are generated through the deprotonation of polymer radical cation.

↓

Polymer structure dependent

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

Counteranion generation

Anions are generated through the reaction of acid generators with secondary electrons.

↓

Acid generator structure dependent

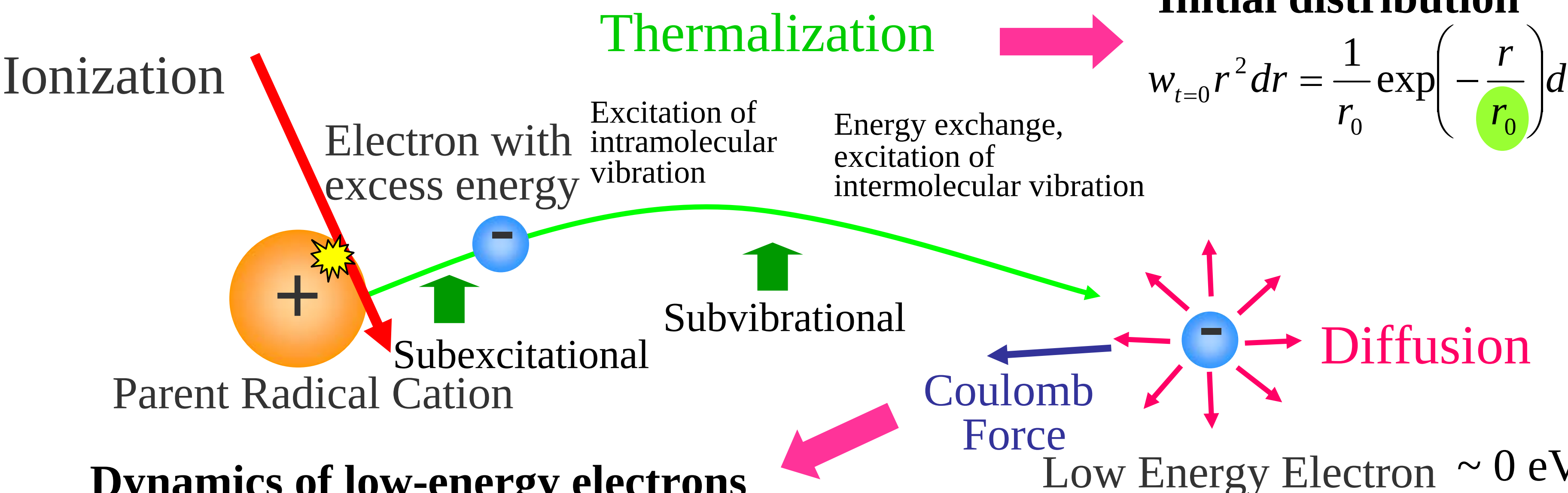
For PHS-based resist,

T. Kozawa et al., J. Photopolym. Sci. Technol. 20 (2007) 577.

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

Generation efficiency of counteranion per ionization

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



Initial distribution

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

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

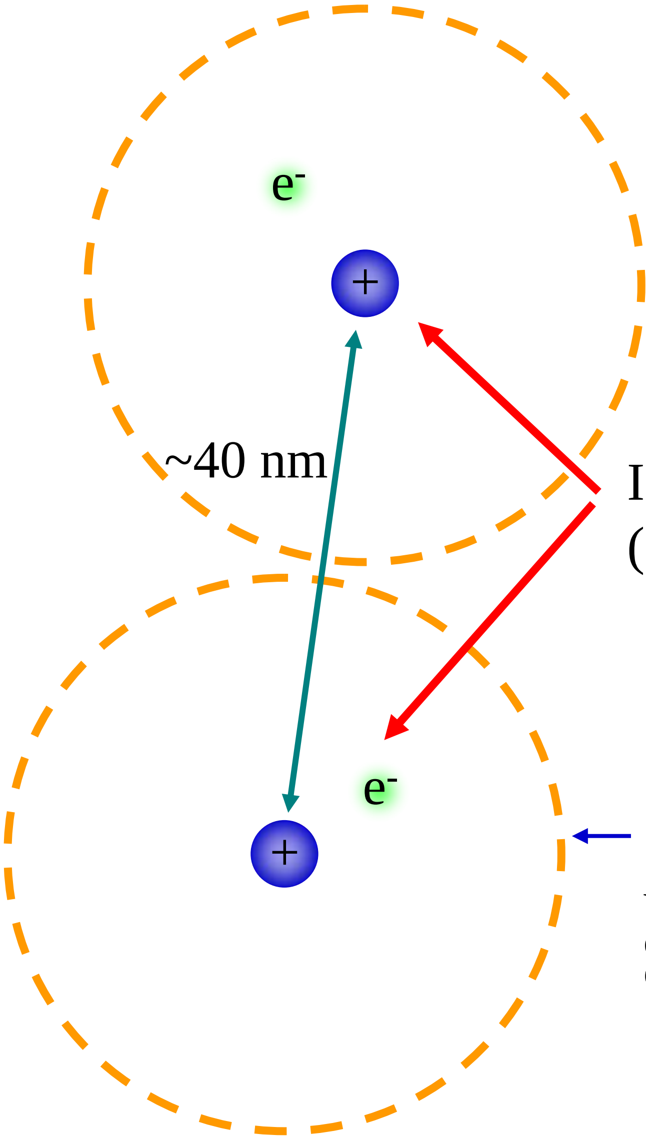
T. Kozawa et al., J. Vac. Sci. Technol. B22 (2004) 3489.

Generation efficiency of counteranion per ionization :

$$\phi_{AG(electron)} = \frac{4\pi \int_0^\infty \int_{r_+}^\infty R_{AG} C_{AG} w r^2 dr d(D_e t)}{\int_{r_+}^\infty w_{t=0} r^2 dr}$$

Difference between EB and EUV

EB



Isolated pairs
(Single spur)

Onsager distance

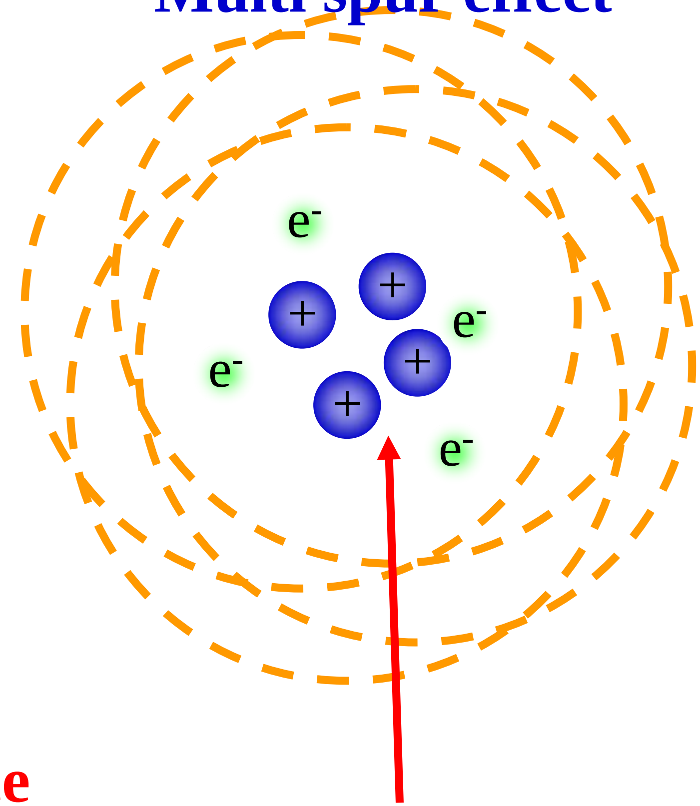
Where the thermal energy of electron correspond to the Coulomb potential.

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

~14 nm in PHS

EUV

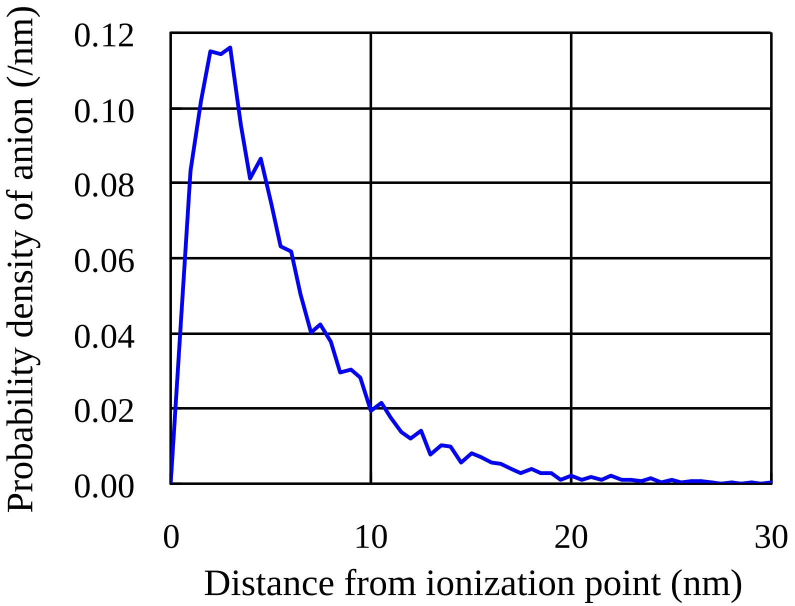
Multi spur effect



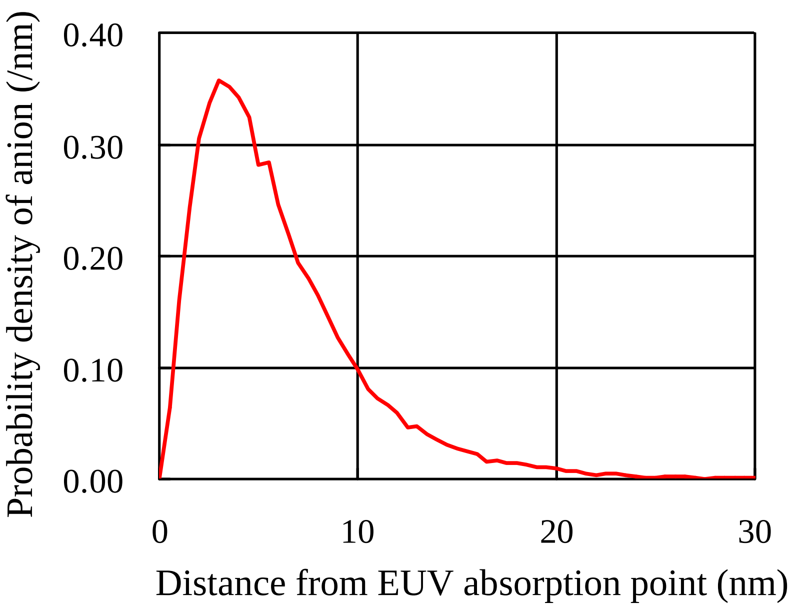
Stronger electric field

T. Kozawa et al. J. Vac. Sci. Technol. B 25 (2007) 2481.

Difference in sensitization distance between EUV and EB



(a) **EB**



(b) EUV

Fig. Probability density of anion generated in PHS with 10 wt% TPS-tf by (a) an electron and (b) an EUV photon.

Sensitization distance (ionization)

EB	EUV
5.6 nm	6.3 nm

Acid generation efficiency (ionization)

EB	EUV
0.74 per ionization	0.62 per ionization
	2.6 per photon

T. Kozawa et al. J. Vac. Sci. Technol. B 25 (2007) 2481.

Quantum yield in chemically amplified resist

$$\phi_{acid} = 2.6\phi_{polymer+} + \phi_{acid(excitation)}$$

Ionization path

Excitation path

$$\phi_{acid(excitation)} \approx 0.02 \sim 0.08\phi_{acid}$$

Deprotonation efficiency of polymer radical cation

Protecting ratio

$$\phi_{polymer+} = 1 + p(\phi_{pg+} - 1)$$

Deprotonation efficiency of protecting group

$$\phi_{pg+} = 0.145 \sim 0.749$$

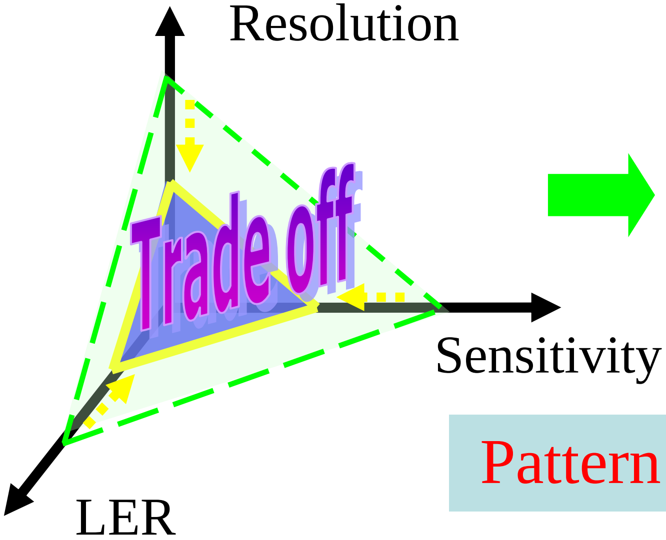
[JJAP 44, 5836 (2005)]

When $p = 0.3$,

$$\phi_{polymer+} = 0.74 \sim 0.92$$

The quantum yield of typical resists is 2.0~2.8 with 10 wt% acid generator loading.

T. Kozawa et al. J. Vac. Sci. Technol. B 25 (2007) 2481.



The increase in pattern formation efficiency is required to simultaneously meet the requirements for resolution, sensitivity, and LER.

Pattern formation efficiency

||

Absorption efficiency of incident energy (absorption coefficient of polymer)

X *Limited by side wall degradation*

Quantum yield of acid

X *Limited by secondary electron emission efficiency*

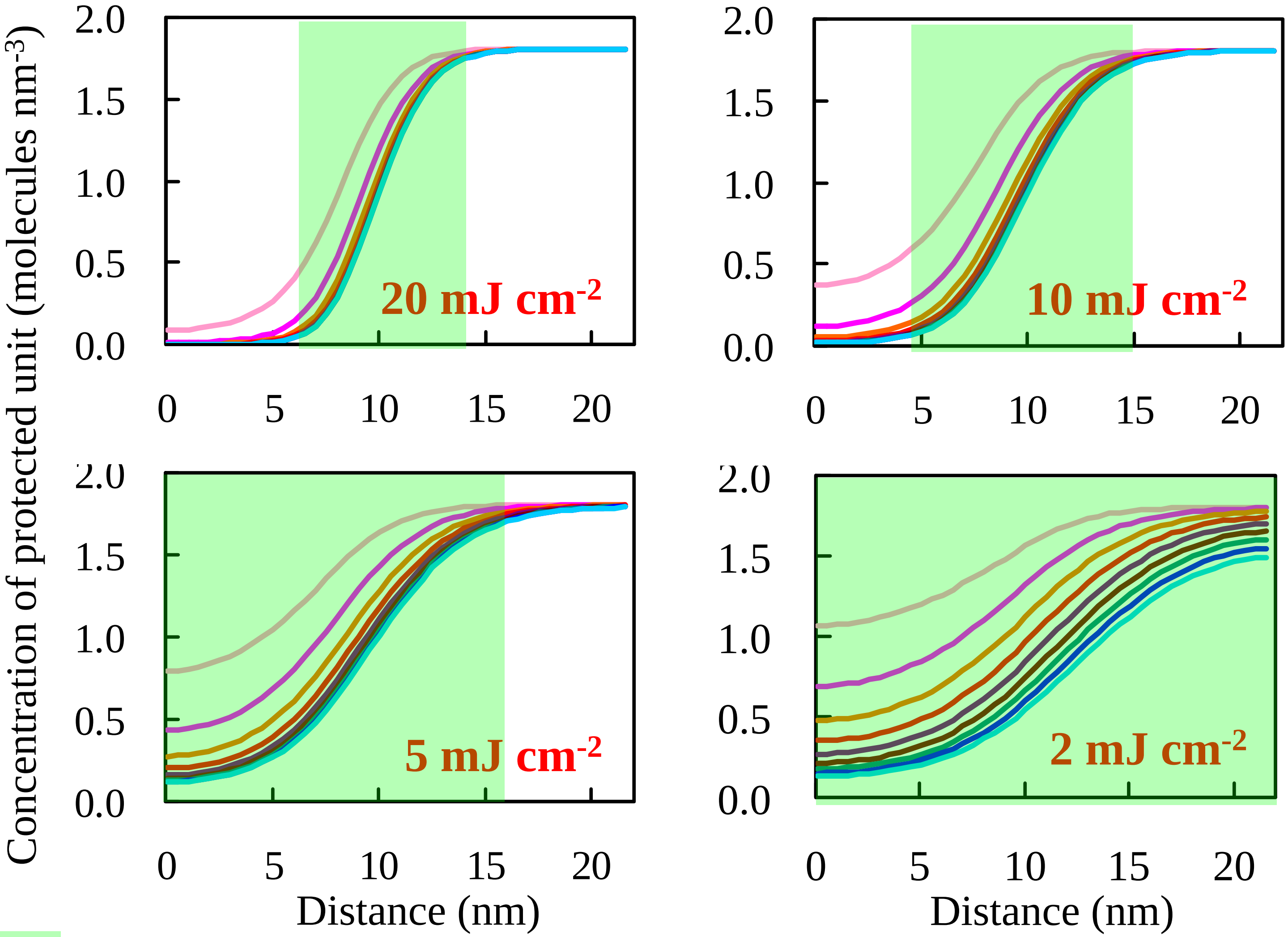
Efficiency of catalytic chain reaction

Limited by diffusion-controlled rate for chemical reaction

T. Kozawa et al. Jpn. J. Appl. Phys. 47 (2008) in press

Limit of PHS-based chemically amplified resist

Latent images of 22 nm line & space



Intermediate region where protected and deprotected units coexist

The width expands with $1/\sqrt{dose}$ dependence.

T. Kozawa et al. Jpn. J. Appl. Phys. 47 (2008) in press