Outgas from EUV Resist Materials Irradiated with EUV and 2 keV electrons
What is difference?

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Radiation Effects on Polymers

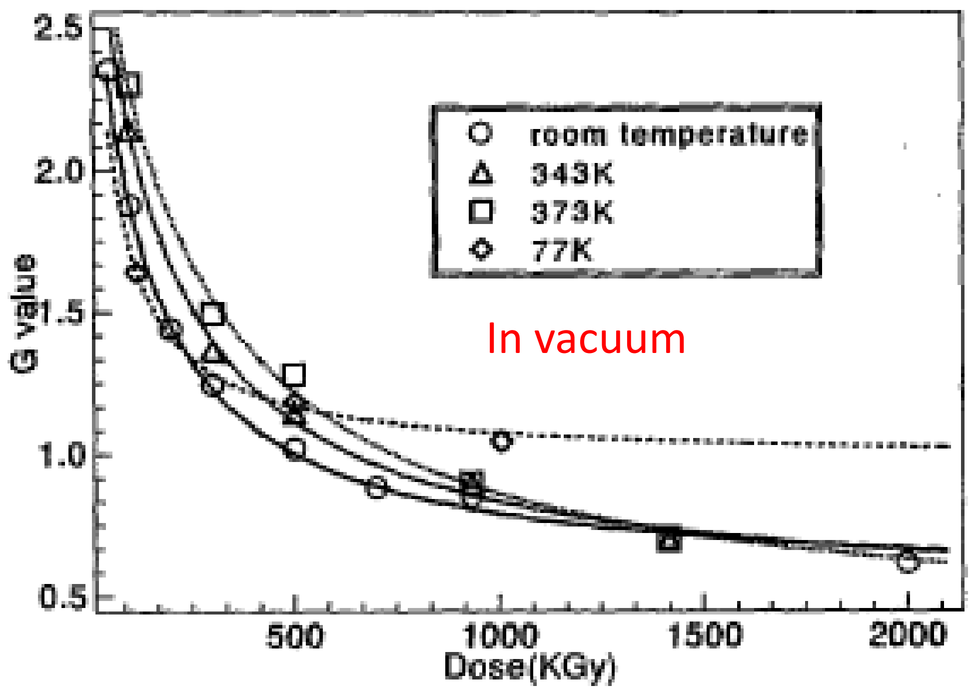
- Long history and so many papers.
- Reactions : crosslinking, scission (main and side chain scission), and others (double bond formation-coloring, branching etc.).
- Radiation resistant materials for nuclear & fusion reactors.
- Industrial use (crosslinking for cables and graft polymerization for new functional materials)

Typical Example of Radiation Effects on Polymers

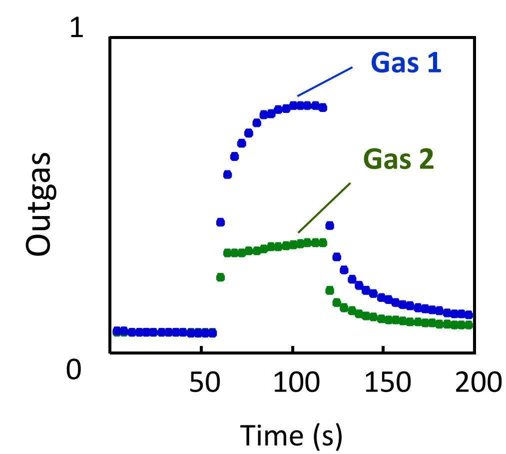
Radiation Effects on Low Density Polyethylene (LDPE)

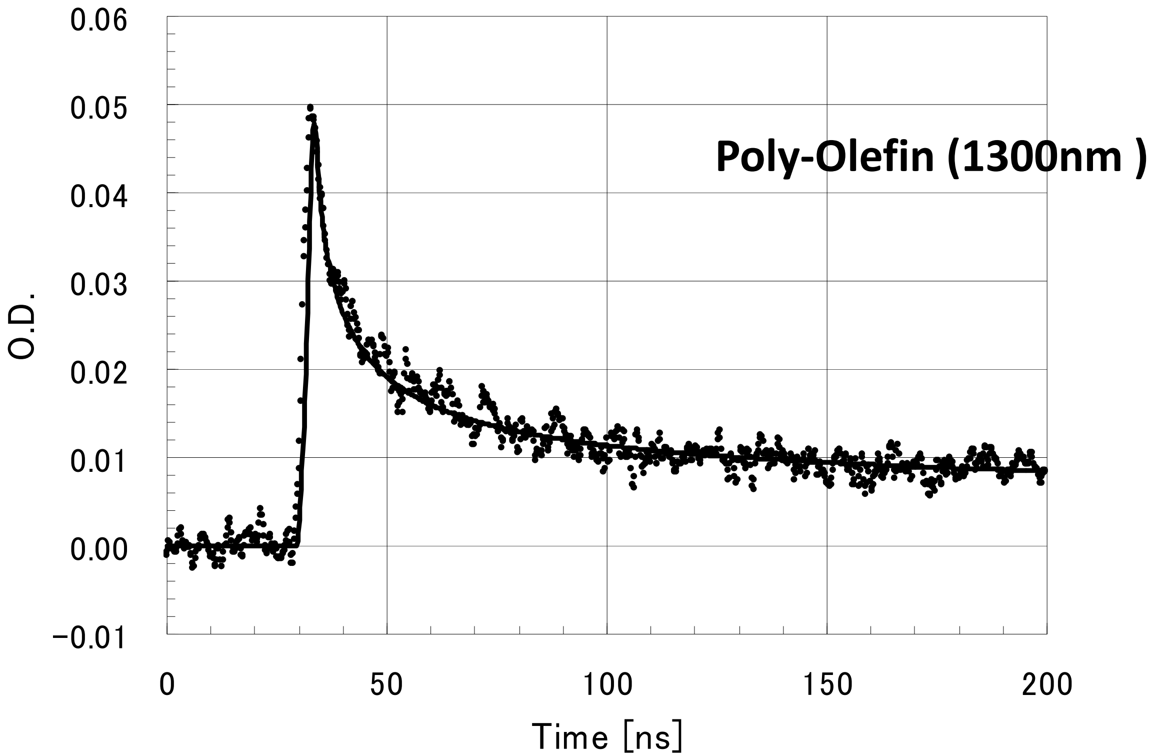
Dose, Temperature, Atmosphere

Dose: mJ/cm2, μC/cm2 in lithography
Dose: J/kg (Gy) in radiation chemistry and general science aera including nuclear science and technology



Dose dependence of the G-value for the yield of the trans-vinylene induced in LDPE by γ-ray irradiation at various temperatures.





Smoluchowski eq.
Initial Distribution
Exponential 6nm
D = 6 x 10-6 cm2/s

Ion recombination (geminate recombination) between electron and positive hole in EB irradiated solid film of polyolefin at 1300 nm (infra-red) at room temperature measured by pulse radiolysis method

S. Tagawa et al.

Important Factors in Radiation-Effects on Polymers in Outgas Problem

- Dose Effects
- Dose Rate (Radiation Intensity) Effects

  Long History for Nuclear Reactor Materials

  Oxidation is the most and only important problem except for heaing.

  Dose rate can be easily controlled by control of EB current.
- LET (Linear Energy Transfer) Effects

  Stopping (S) Power Effects
- Atmosphere (Temperature Effects, O_2 Effects etc.) Effects

Dose: mJ/cm2, μC/cm2 in lithography

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Energy Absorption Process

Charged Particle; Stopping Power (LET) Electron Density

$$\left(-\frac{dE}{dx}\right)_{\text{ion}} = \frac{4\pi e^4}{mc^2}(N_{\text{tar}}Z_{\text{tar}})\left(\frac{Z_{\text{eff}}^2}{\beta^2}\right)\ln\frac{2mc^2\beta^2}{I}$$

EUV: 92.5 eV light; Lambert Law

Absorption Coefficients of Atoms in Resists

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

Absorption coefficient (**α**)

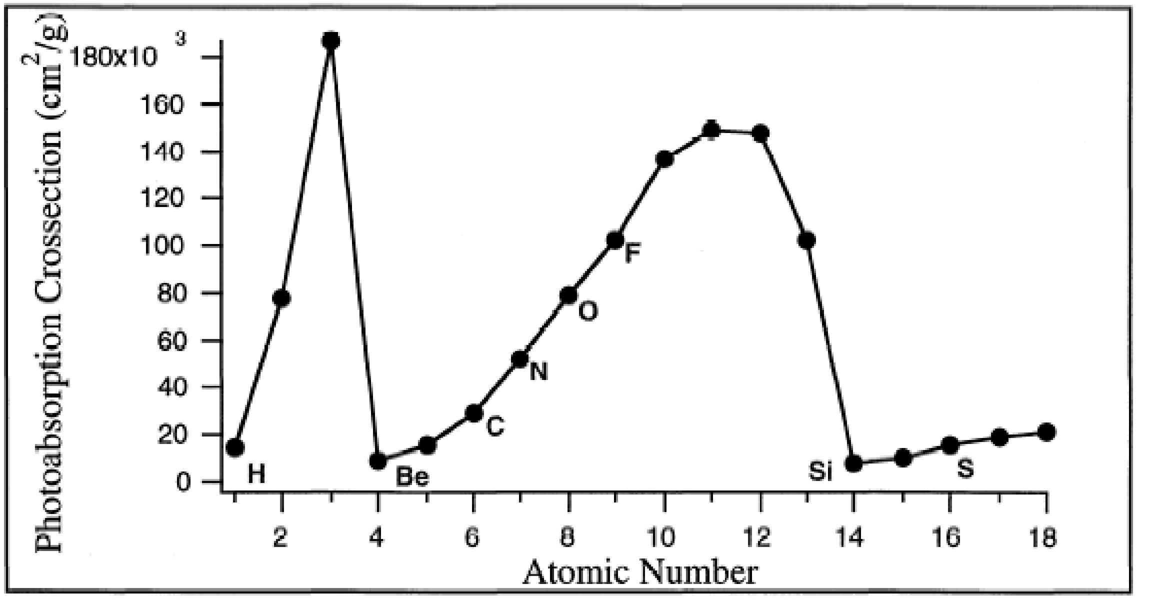


Figure 1: Elemental absorption cross-sections at 13.4 nm wavelength. Elements commonly found in photoresist materials are H, C, N, O, F, and S.

P. Dentinger et al., SPIE 3997 (2000) 588.

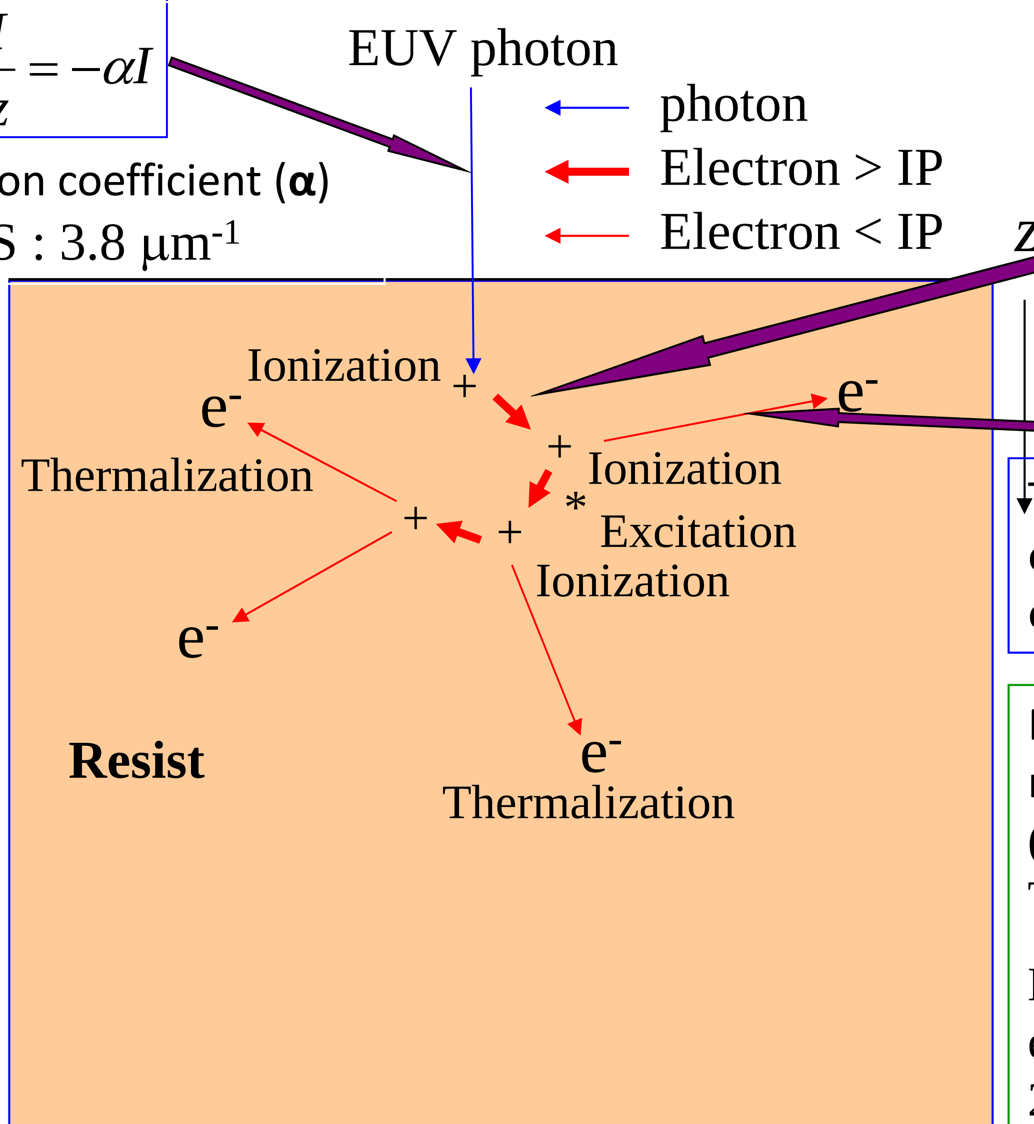
Interaction of EUV photon with CARs -spatial distribution-

Intensity of EUV (I)

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

Absorption coefficient (**α**)

PHS : 3.8 μm^{-1}



Inelastic mean free path

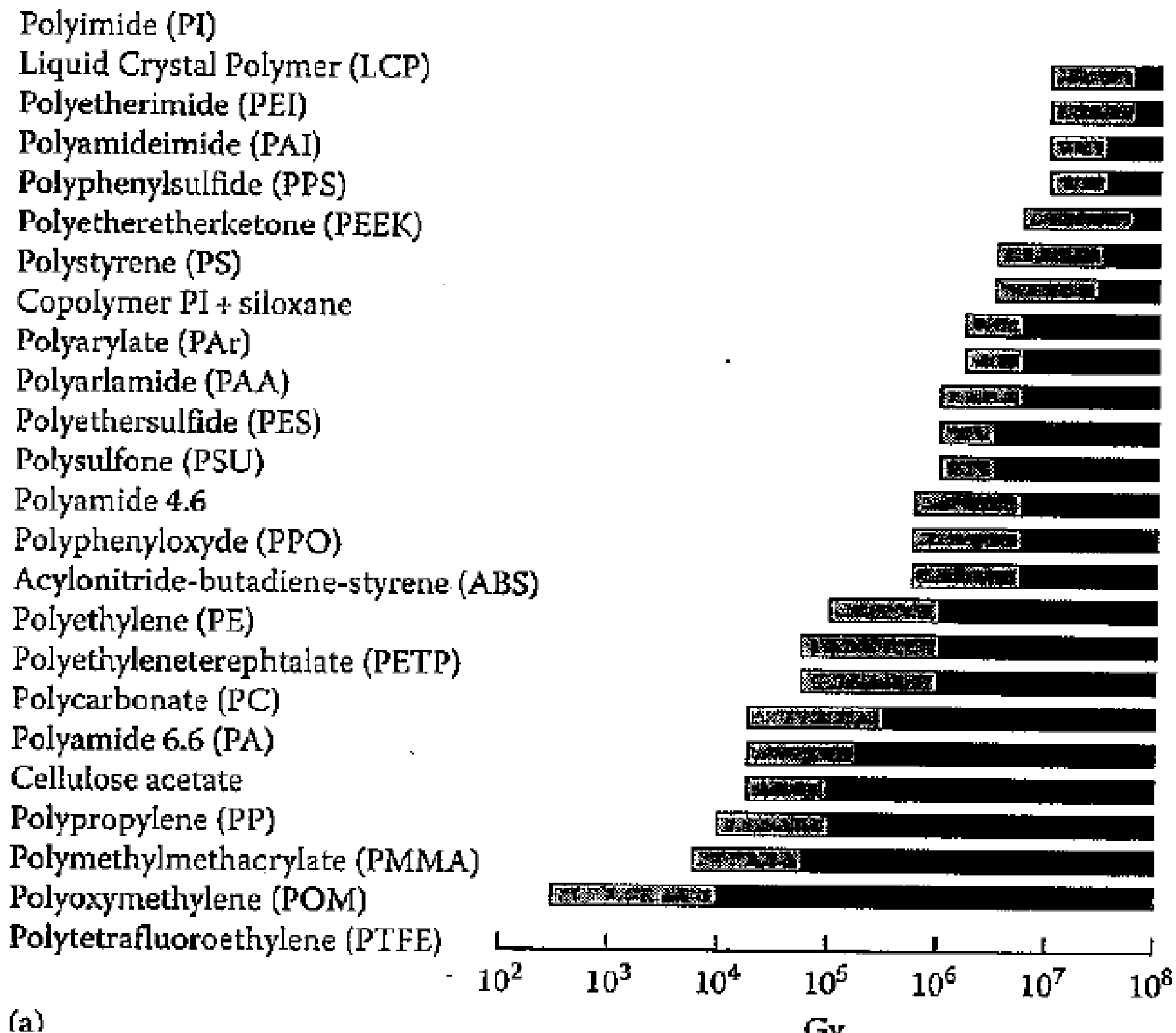
<1 nm mean free path at electron with energy > IP

Thermalization Length 4.0 nm for PHS

The number of secondary electrons is estimated expermentally. 4.2 for PHS

PHS with 10 wt% TPS-tf Acid molecules per photon: 2.6 (Kozawa et al. J.Vac.Sci. Tecnnol.,B25(2007) 2481)

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



General classification of radiation resistance. (a) Rigid thermoplastics.

Mild to moderate damage, utility is often satisfactory

Moderate to severe damage, use not recommended

(Reprinted from Tavlet, M. et al., Compilation of radiation damage test data, Part II, 2nd

Dose: mJ/cm2, μC/cm2 in lithography

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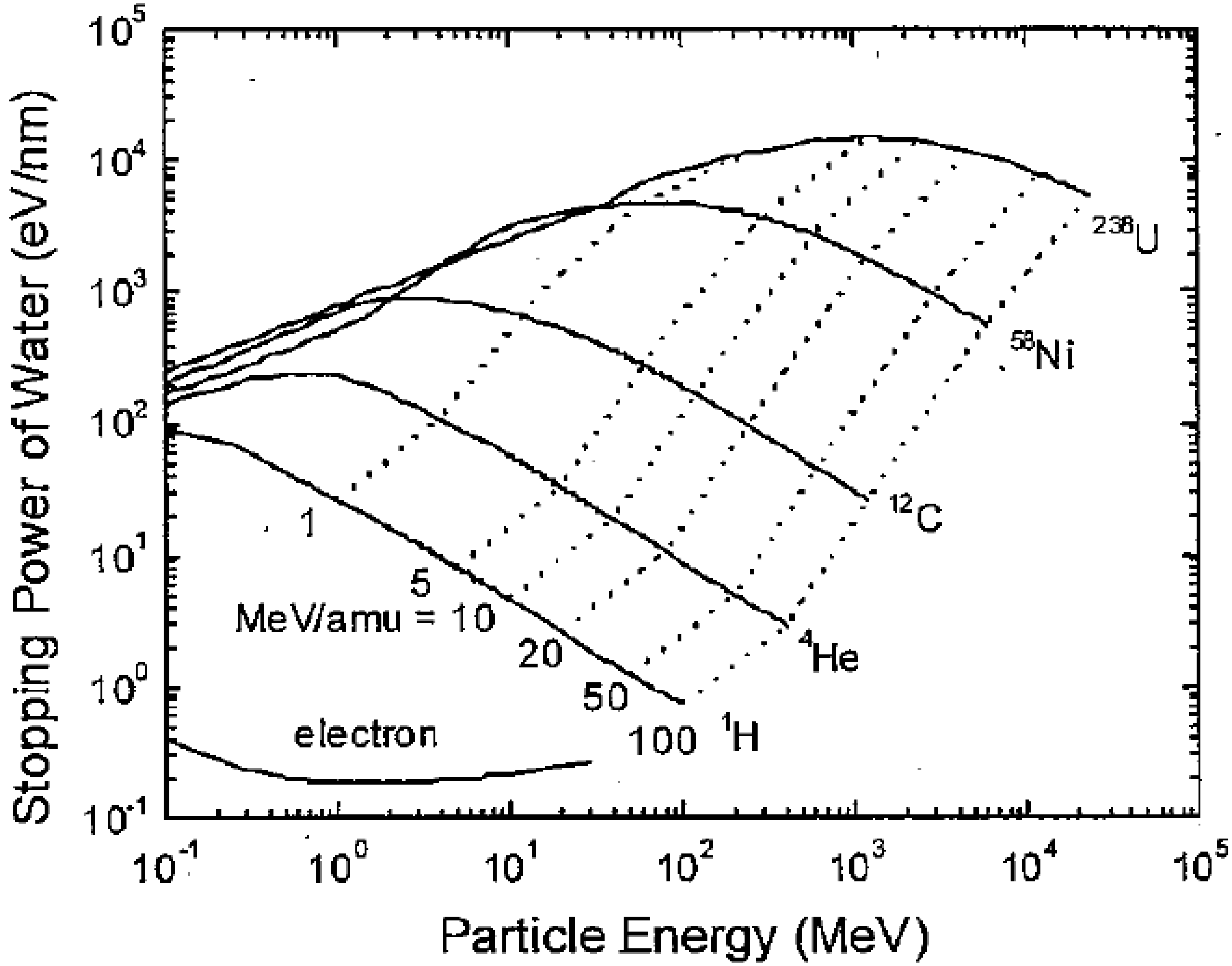
Stopping Power (-dE/dx)、LET(-dE/dx)



Stopping power, $-\mathrm{d}E/\mathrm{d}x$, of some heavy ions and electrons in water as a function of energy. The dotted lines show the stopping power for heavy ions of equal velocity.

Jay. A. LaVerne

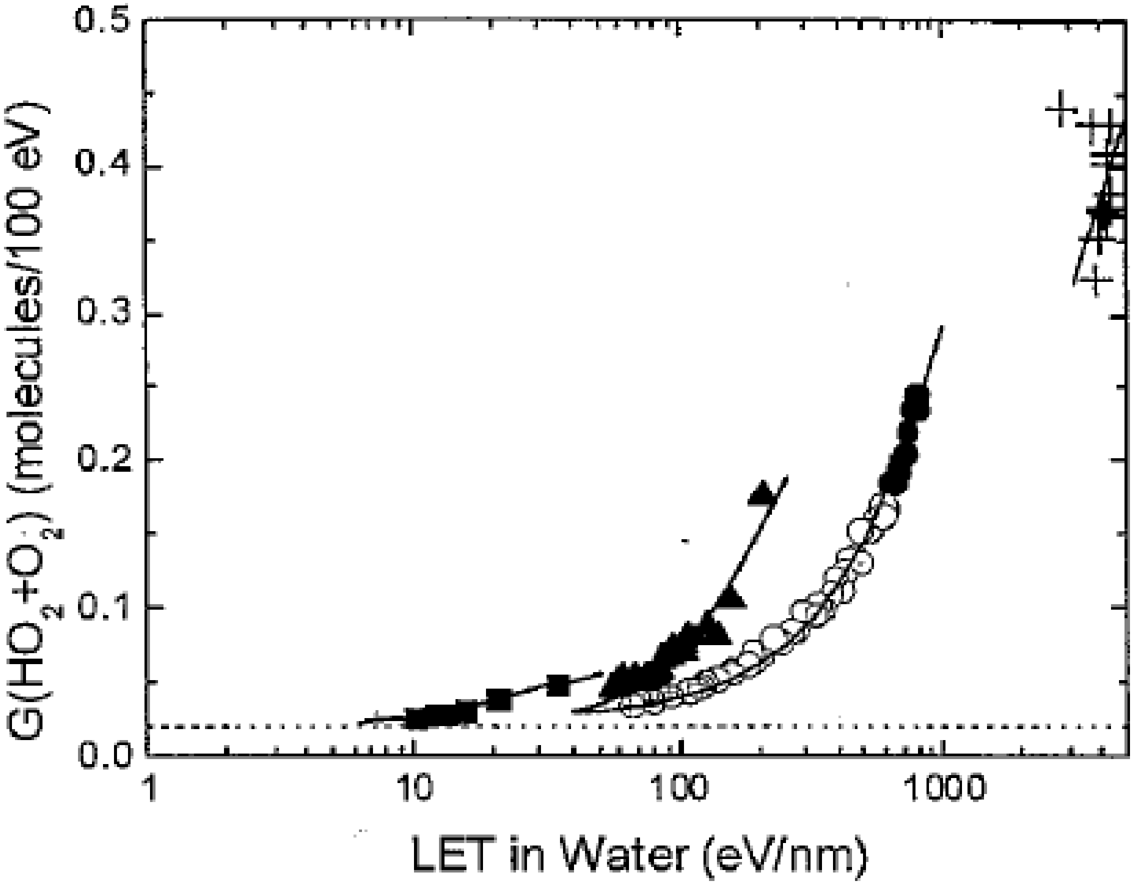


Figure 7 Track average yields of HO_2 as a function of heavy ion LET: (■,▲,●) ^{1}H, ^{4}He, and ^{12}C, Ref. 75; (○) ^{12}C, Ref. 94; (⊙) ^{12}C, Ref. 96; (+) ^{58}Ni, Ref. 95. The dotted line is the limiting fast electron yield of 0.02 [123].

Conclusion

Important Factors in Radiation-Effects on Polymers in Outgas

- Dose Effects

Dose: mJ/cm2, µC/cm2 in lithography
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- Dose Rate (Radiation Intensity) Effects

Long History for Nuclear Reactor Materials
(Oxidation is the most and only important problem)
Dose rate can be easily controlled by control of EB current.

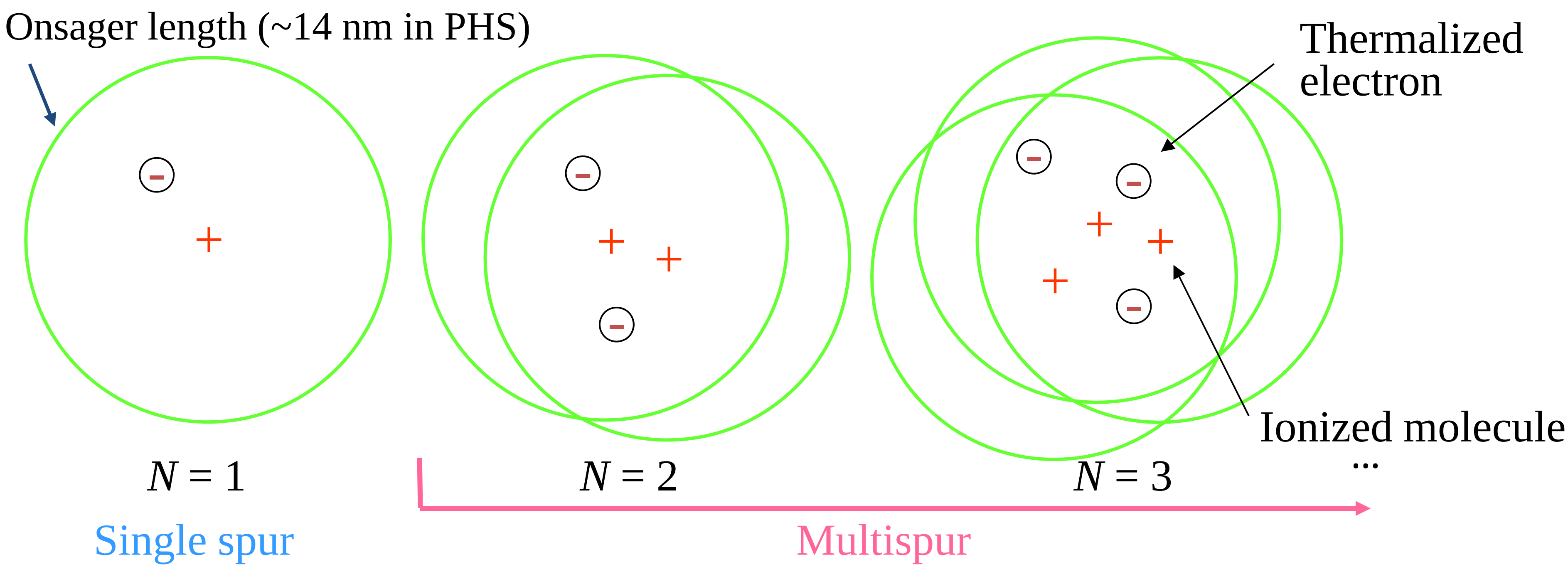
- LET (Linear Energy Transfer) Effects

Stopping (S) Power Effects

- Atmosphere (Temperature Effects, O_2 Effects etc.)

- Generally speaking, difference between EUV and 2 keV exposure in outgas problems is small and controled, although there is difference.

Initial configuration of reactive intermediates



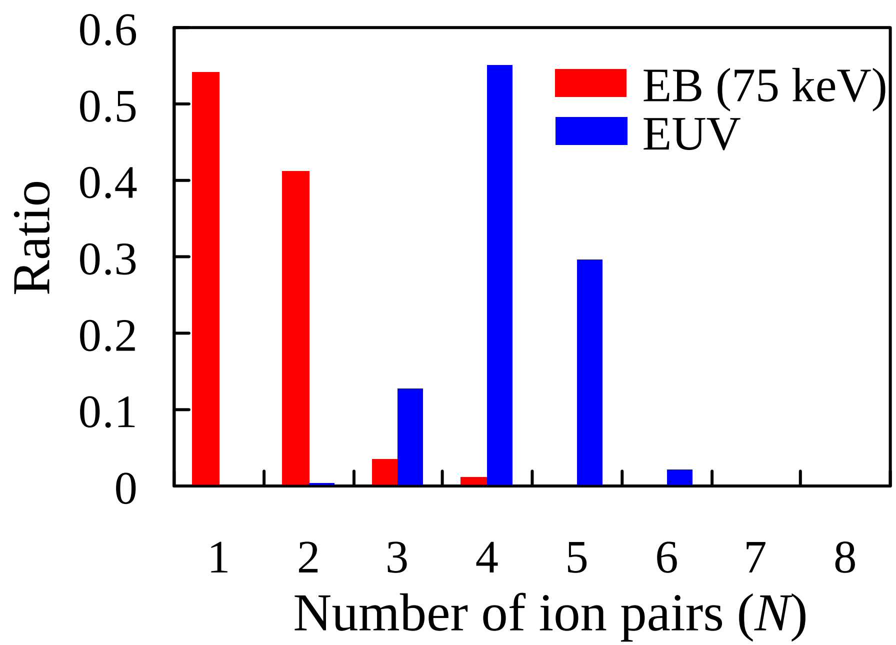
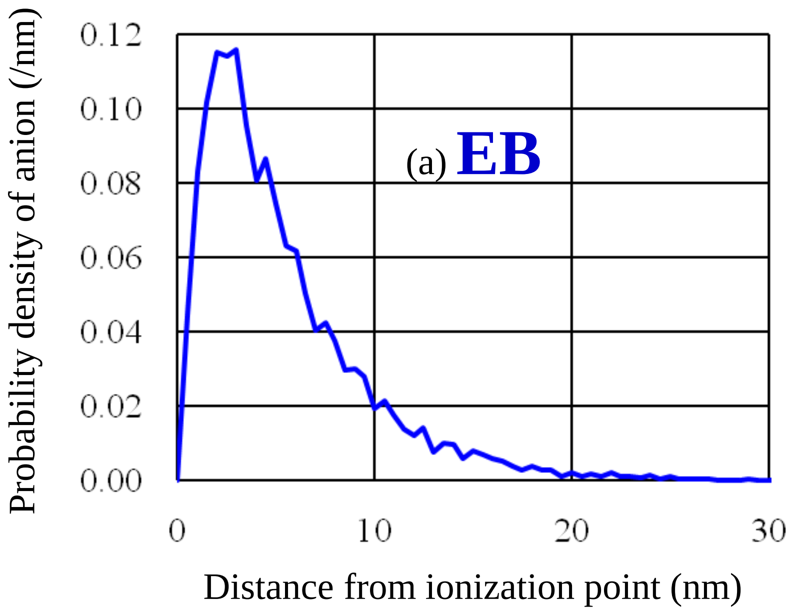


Fig.8 Distribution (histogram) of overlapped spurs in EB and EUV resists. The average number is 1.5 for EB and 4.2 for EUV. The energy of incident electrons is 75 keV.

T. Kozawa et al., Jpn. J. Appl. Phys. 48 (2009) 056508.

Difference in sensitization distance between EUV and EB



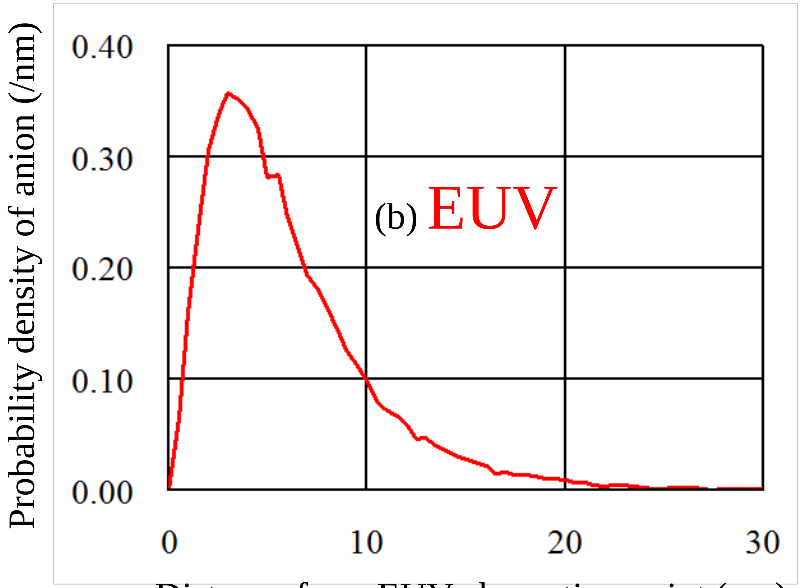


Fig. Probability density of anion generated in PHS with 10 wt% TPS-tf by (a) an electron and (b) an EUV photon.

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

G(acid) = 3.3 (3.3 acids per 100 eV)

2.6 acids per one photon(92.5 eV) in PHS

Kozawa and Tagawa, J.Vac.Sci.Tecnnol.,B25(2007) 2481

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

Experimental value: 2.5 Hirose et al., Jap.J.Appl. Phys, Part 2 Let. & Express Let.,46,L979(2007)

Acid yield in chemically amplified resist (PHS)

Stopping power in PHS : 57.8 eV/100 nm at 75 keV
G value of ionization in organic materials : 5±1 (per 100 eV absorbed energy)
Acid generation probability : 0.68 (5wt% TPS-tf)