Sensitization and reaction mechanisms of ZrO_2 nanoparticle resist used for extreme ultraviolet lithography

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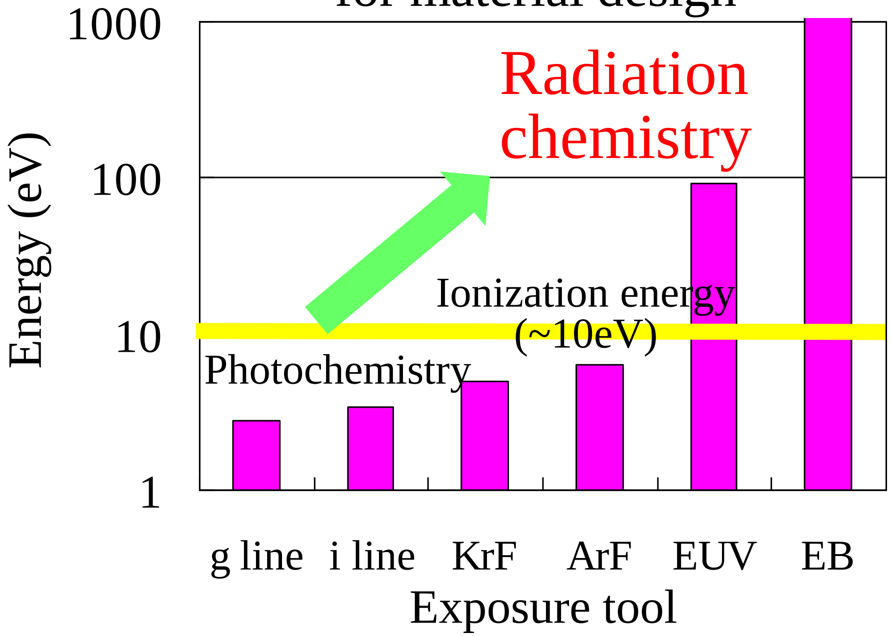
Lithography roadmap

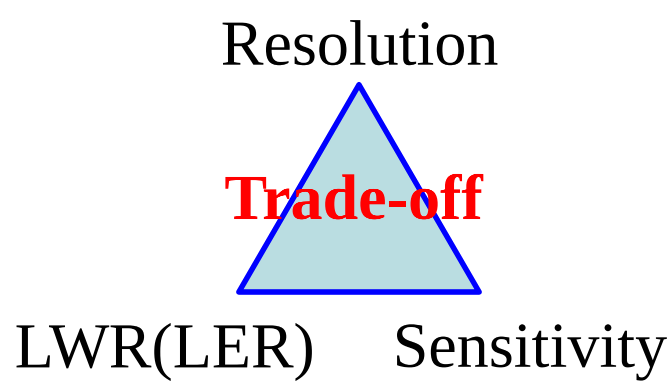
Year	2001	04	07	10	13	16	19	22	25	28
Line width (nm)	130	90	65	45	28	22	17	13	10	7.7
LWR (nm)					2.4	1.8	1.4	1.1	0.8	0.6
Lithography solutions	KrF 248nm	ArF 193nm		ArF immersion (+DP) 193nm			EUV 13.5nm			
	EB for mask production									

Two keywords in the development of resist materials and processes

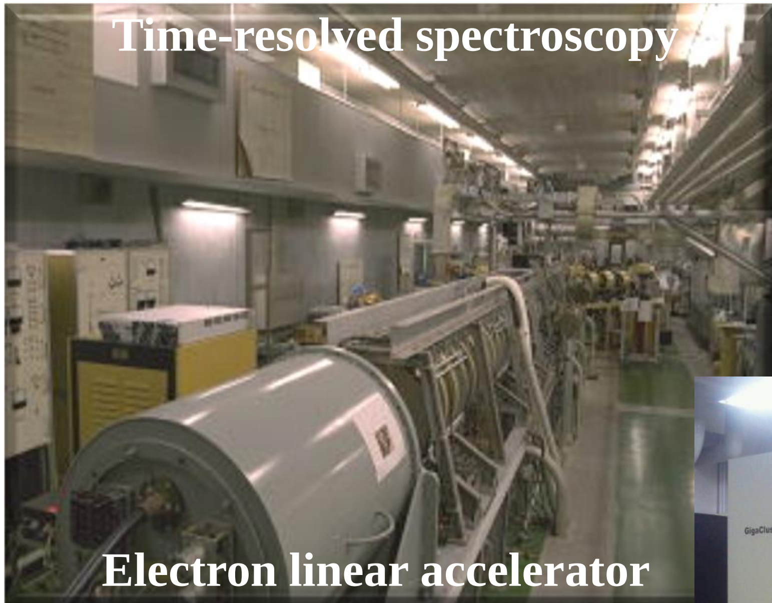
Transition of basic science for material design

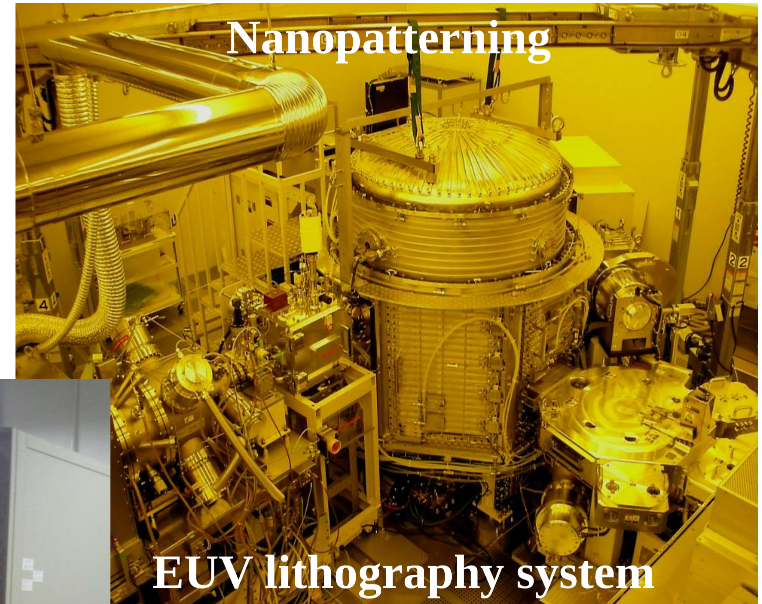


Trade-off relationships between resolution, LWR, and sensitivity



Strategy for development of resist materials





Ultrashort electron beam
Time resolution **<1 ps**
Survey of elementary reactions
Integration of elementary reactions

High-quality optical image
Spatial resolution **<20 nm**
Analysis of SEM images
Resolution, LER/LWR, Sensitivity

Modeling

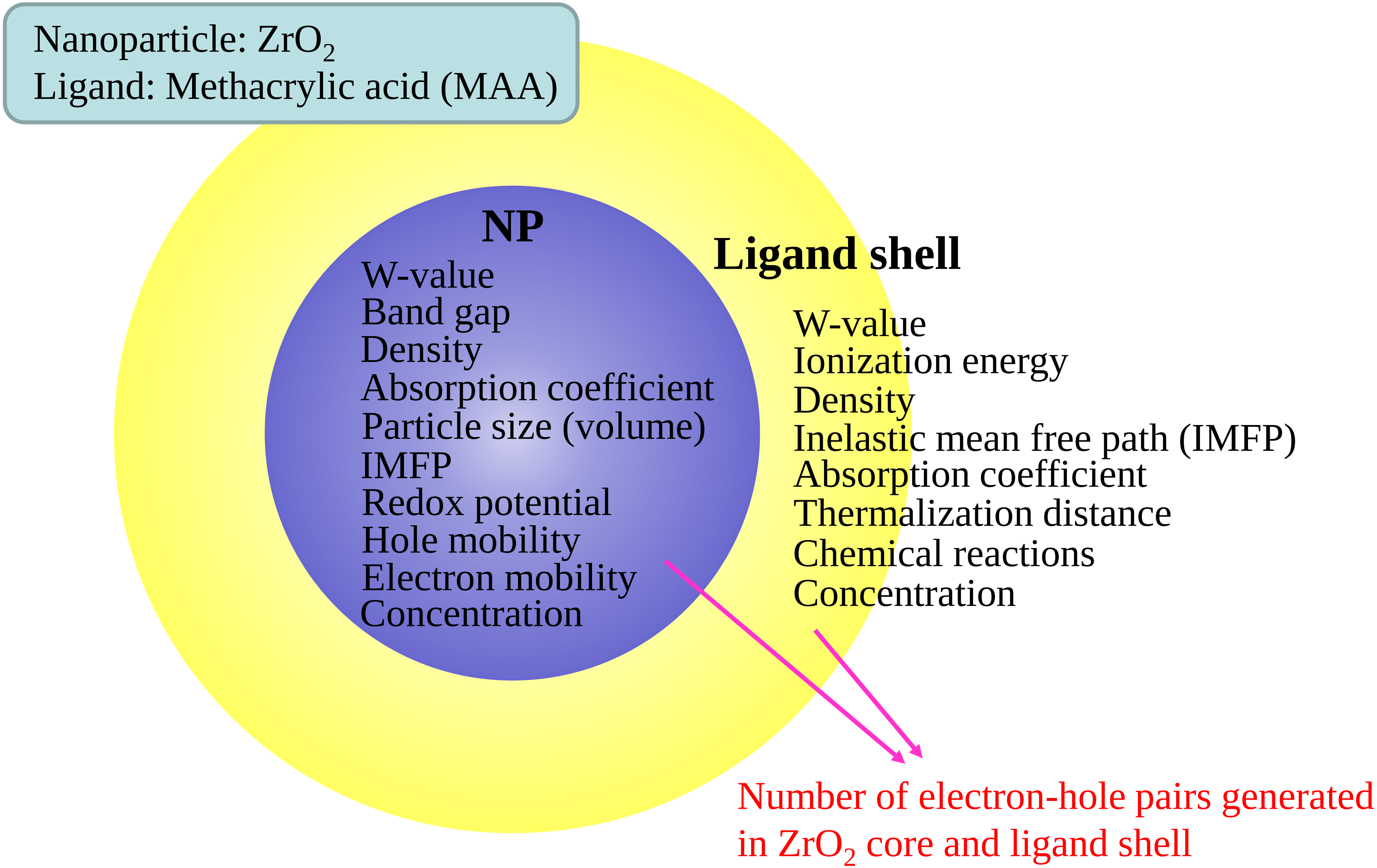
Patterning information

Inverse analysis

Elucidation of reaction mechanism in real materials and extraction of resist parameters

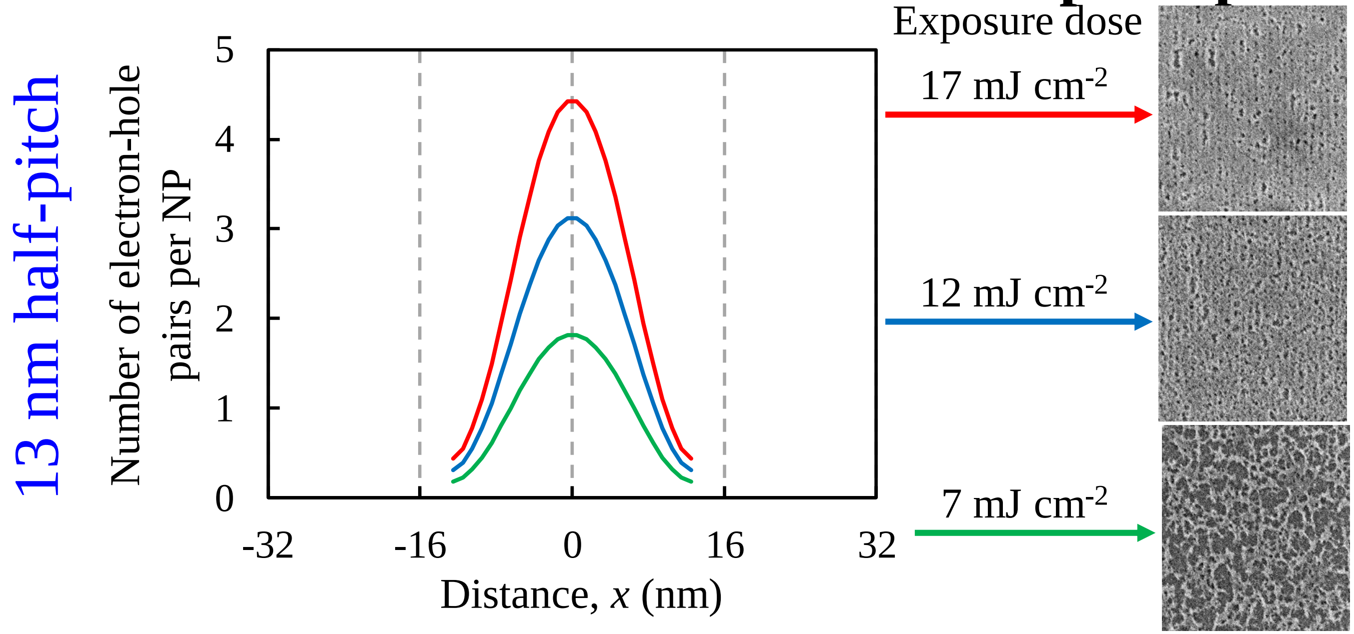
Material design
Acceleration of development cycle

Pattern formation in metal oxide nanoparticle resist



T. Kozawa, J. J. Santillan, and T. Itani, "Electron–hole pairs generated in ZrO_2 nanoparticle resist upon exposure to extreme ultraviolet radiation", Jpn. J. Appl. Phys. **57**, 026501 (2018).

Distribution of number of electron-hole pairs per NP with ligand shell (ZrO_2 ratio 0.5)



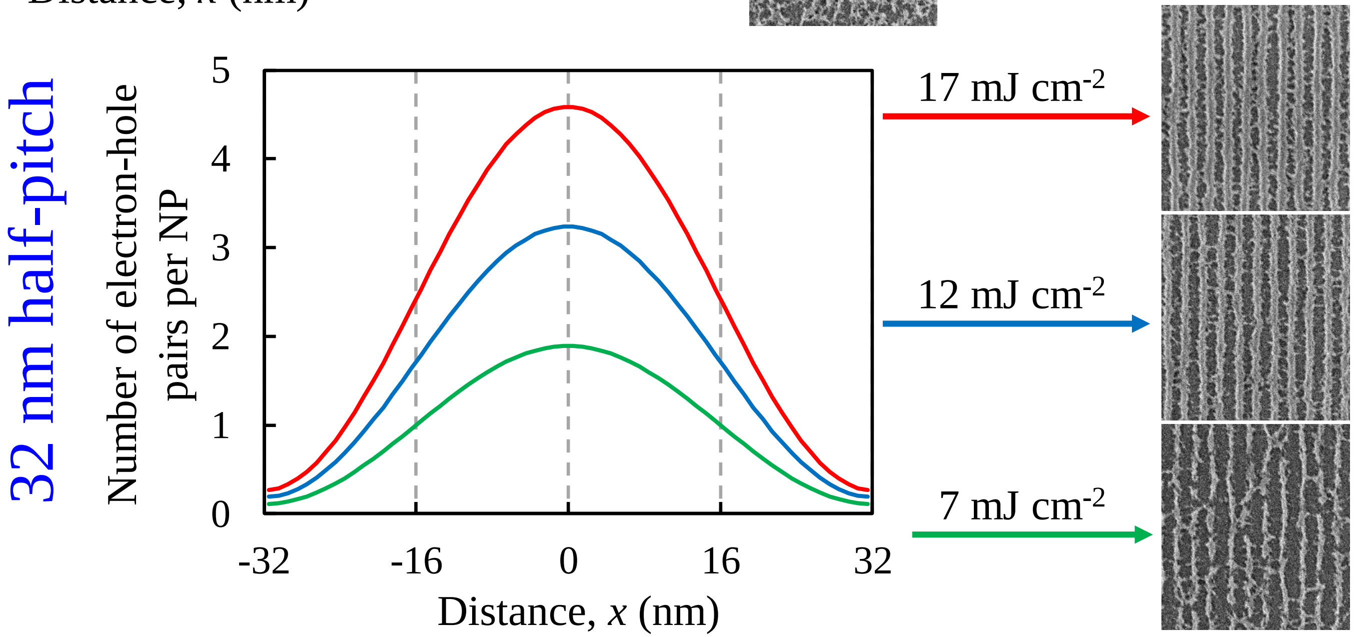


Fig. Distribution of sum of the numbers of electron-hole pairs in zirconia core and the closest MAA shell (ZrO_2 ratio 0.5).

Threshold for insolubilization (ZrO_2 ratio 0.5)

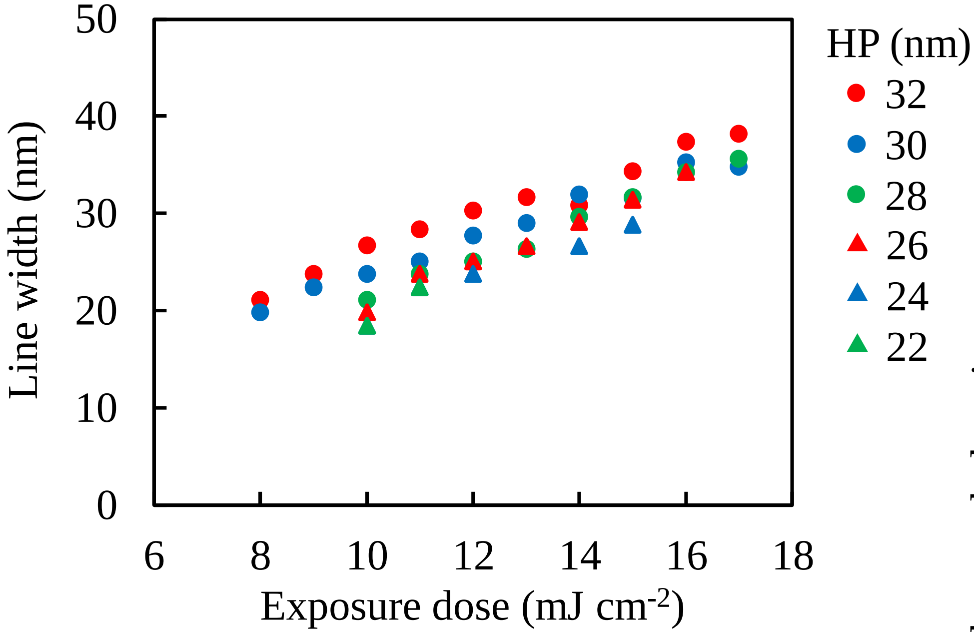


Fig. Dependence of line width on exposure dose and half-pitch.

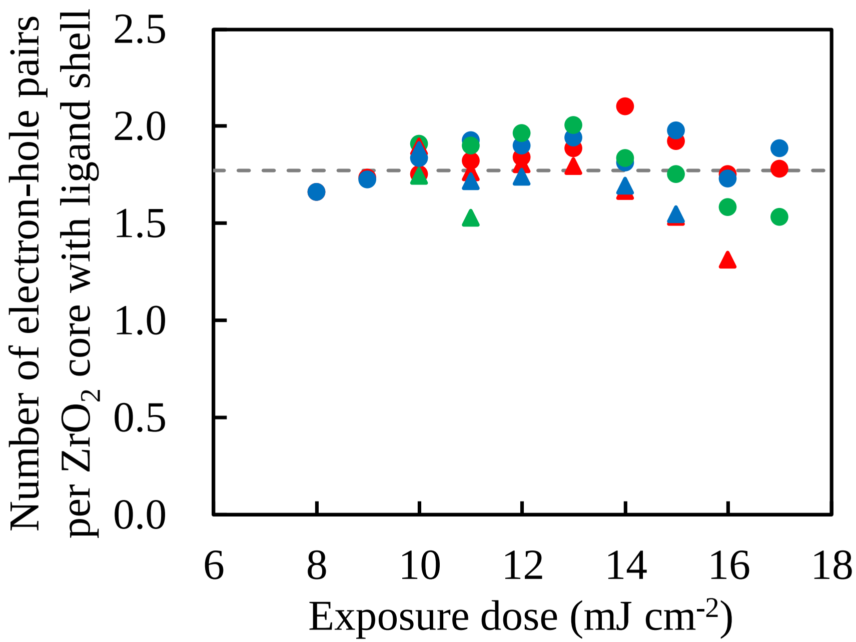


Fig. The number of electron hole pairs at the boundary between lines and spaces.

Average at boundary between lines and spaces: 1.77 electron-hole pairs

Threshold for insolubilization

Both electron and hole availabilities are unknown.

Relationship between LER and chemical gradient (ZrO_2 ratio 0.5)

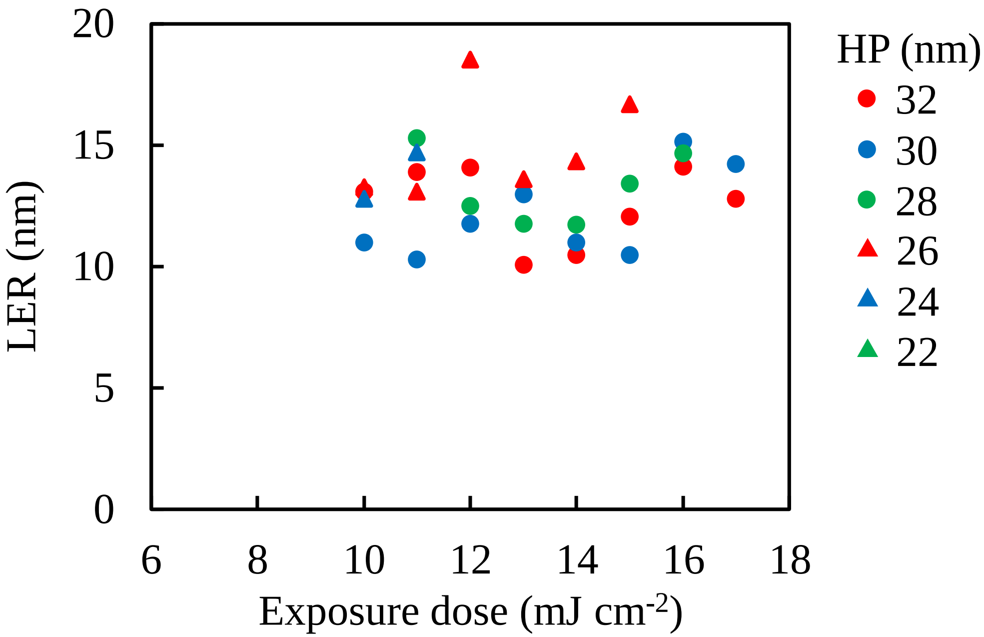


Fig. Dependence of LER on exposure dose and half-pitch.

LER is considered to be inversely proportional to the chemical gradient (d*N*/d*x*) in the right chemical system.

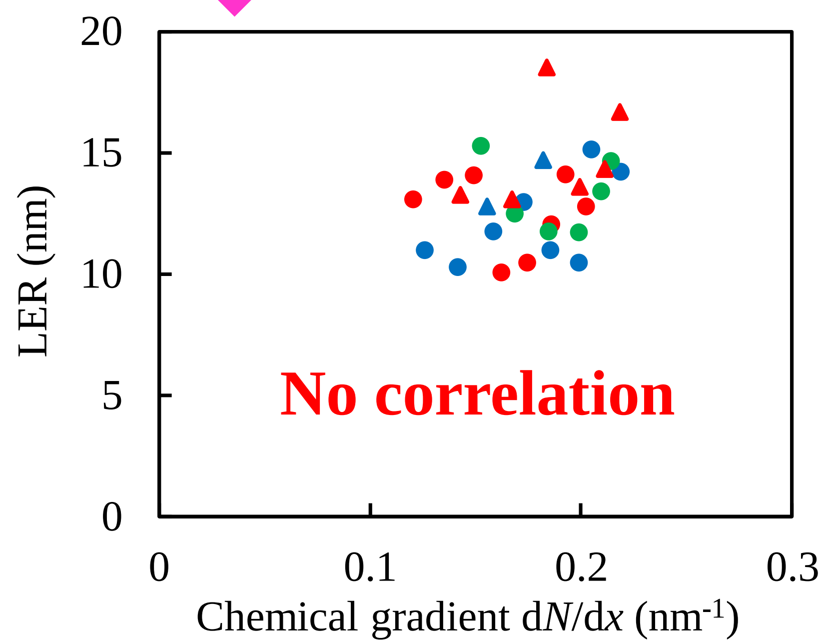


Fig. Relationship between d*N*/d*x* and LER. *N* is the sum of the numbers of electron-hole pairs in zirconia core and MAA ligand shell.

Chemical system (reaction mechanism) has not been optimized.

Electron-hole pair yield

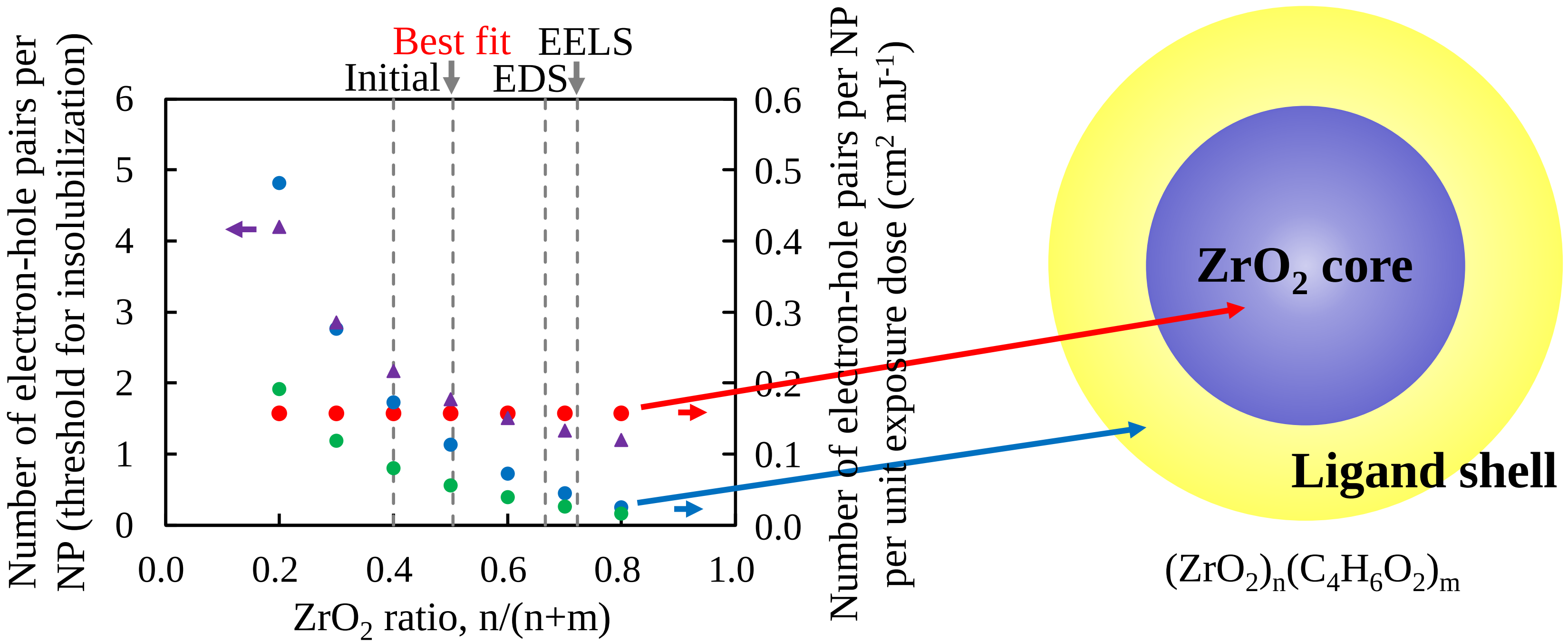


Fig. Dependence of threshold for insolubilization and electron-hole pair yield on ratio of ZrO_2.

The number of electron-hole pairs generated upon exposure to 1 mJ cm^{-2} EUV radiation

In a ZrO_2 core : 0.16

In a ligand shell : 0.04-0.17

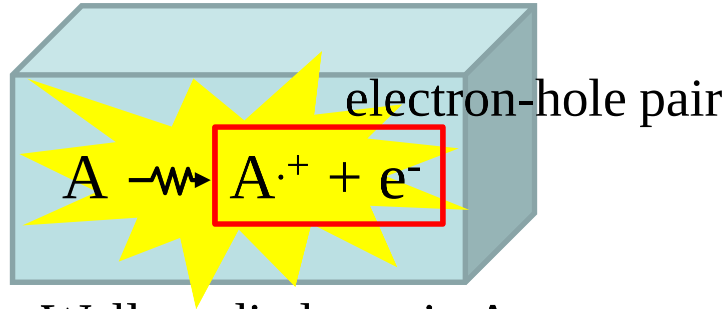
The efficient use of electrons and holes are essential to the design of chemical system.

Pulse radiolysis for study of elementary reactions

1. Generation of electron-hole pairs in well-studied matrix A (H_2O or CH_2Cl_2)

Electron linear accelerator

Ultrashort EB pulse



Well-studied matrix A

2. Study of reaction of electron-hole pairs with target molecules B (MAA)

Reaction of electrons

$$H_2O \rightsquigarrow H_2O^{\cdot +} + e^-$$
$$H_2O^{\cdot +} + H_2O \longrightarrow H_3O^+ + OH^{\cdot}$$
$$B + e^- \longrightarrow B^{\cdot -}$$

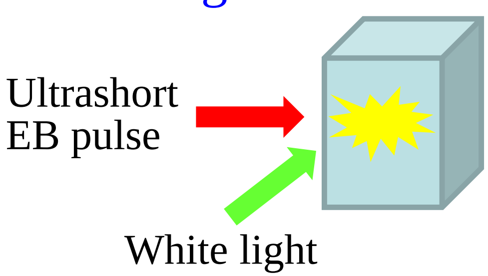
Elimination of reactive hole species

Reaction of holes

$$CH_2Cl_2 \rightsquigarrow CH_2Cl_2^{\cdot +} + e^-$$
$$CH_2Cl_2 + e^- \longrightarrow CH_2Cl^{\cdot} + Cl^-$$
$$B + CH_2Cl_2^{\cdot +} \longrightarrow B^{\cdot +} + CH_2Cl_2$$

Elimination of electrons

3. Detection and tracking of intermediates (e^-, $B^{\cdot -}$, or $B^{\cdot +}$)



Time-resolved spectroscopy with white analyzing light

Reaction of ligands with electrons

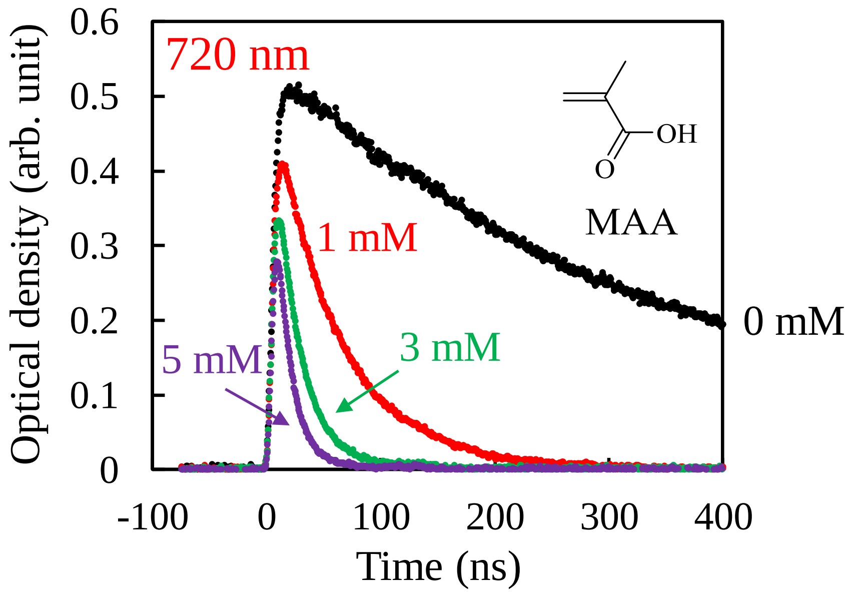


Fig. Kinetic trace of hydrated electrons obtained in the pulse radiolysis MAA solution in water.

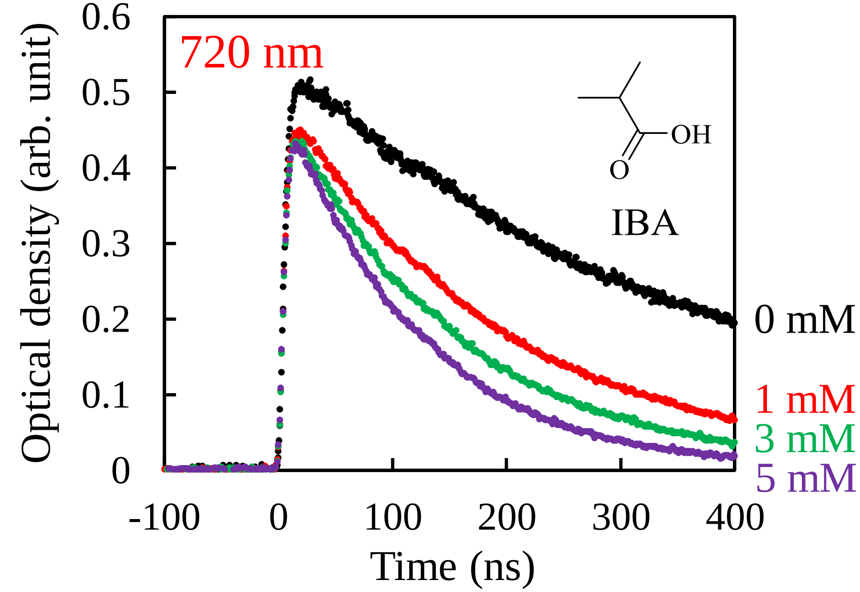
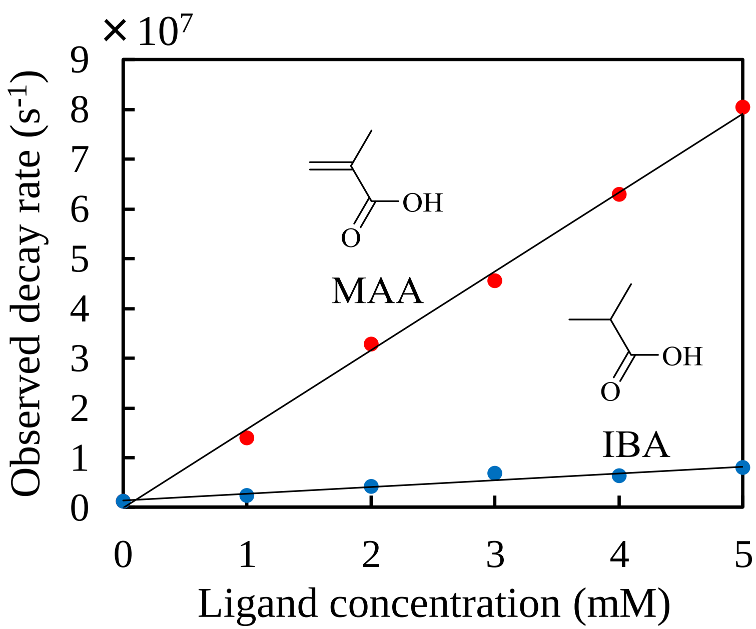


Fig. Kinetic trace of hydrated electrons obtained in the pulse radiolysis IBA solution in water.



Rate constant for the reaction with hydrated electrons

$$B + e^{-} \rightarrow B^{\cdot -}$$

MAA: 1.59×10^{10} $M^{-1}s^{-1}$

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IBA : 1.37×10^{9} $M^{-1}s^{-1}$

Decomposition of MAA anion radicals

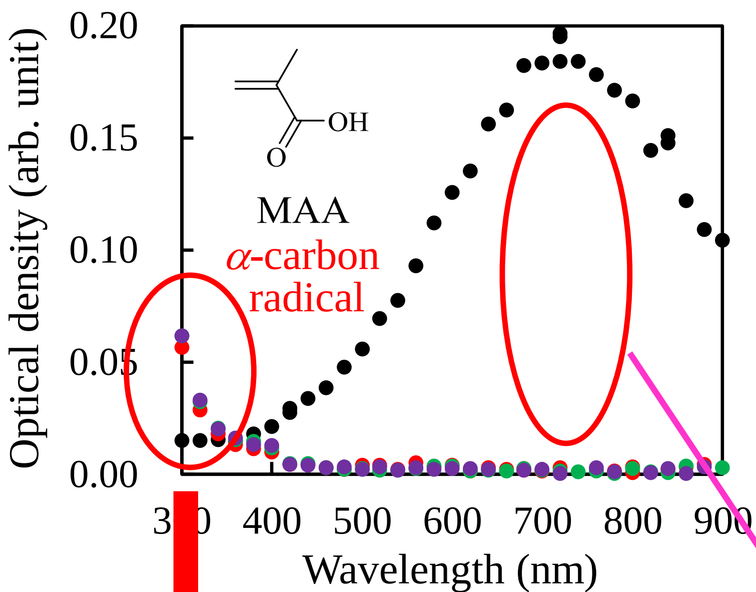


Fig. Transient absorption spectra obtained in the pulse radiolysis of MAA solution in water at 400 ns after an electron pulse.

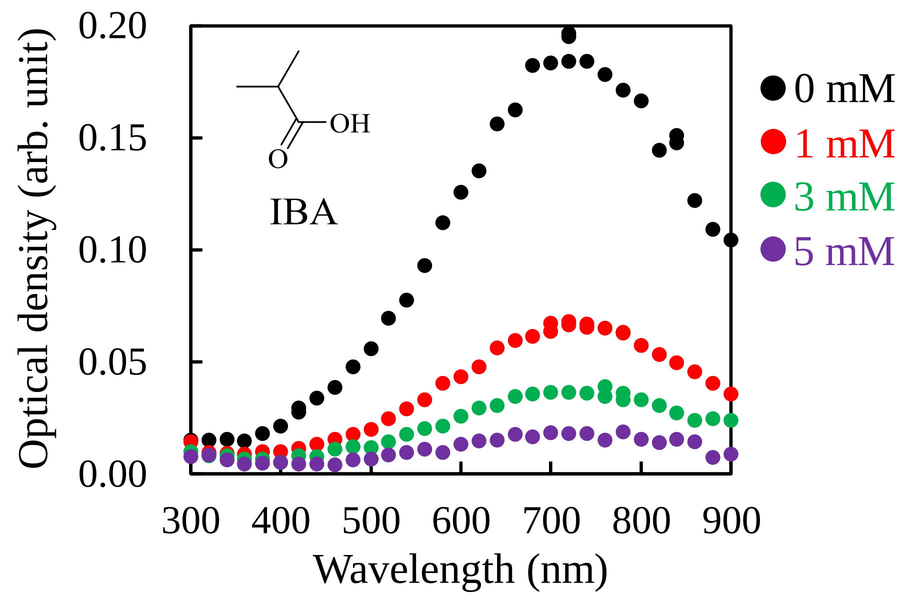
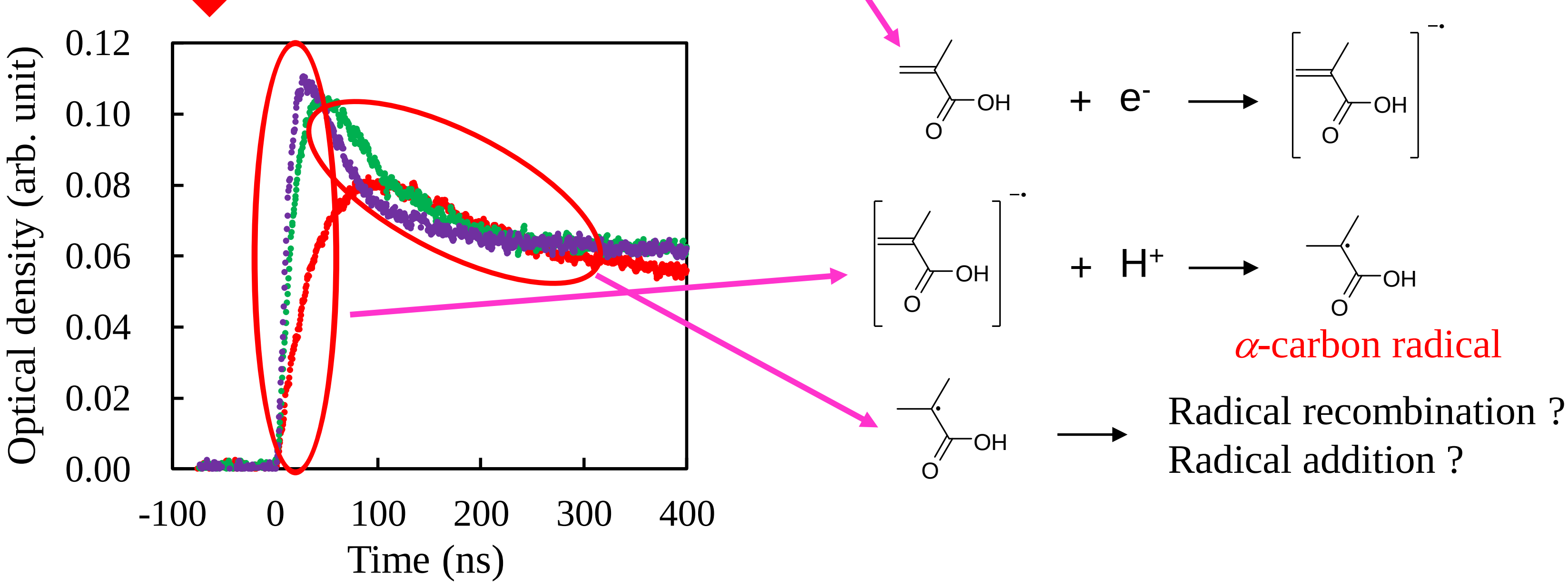
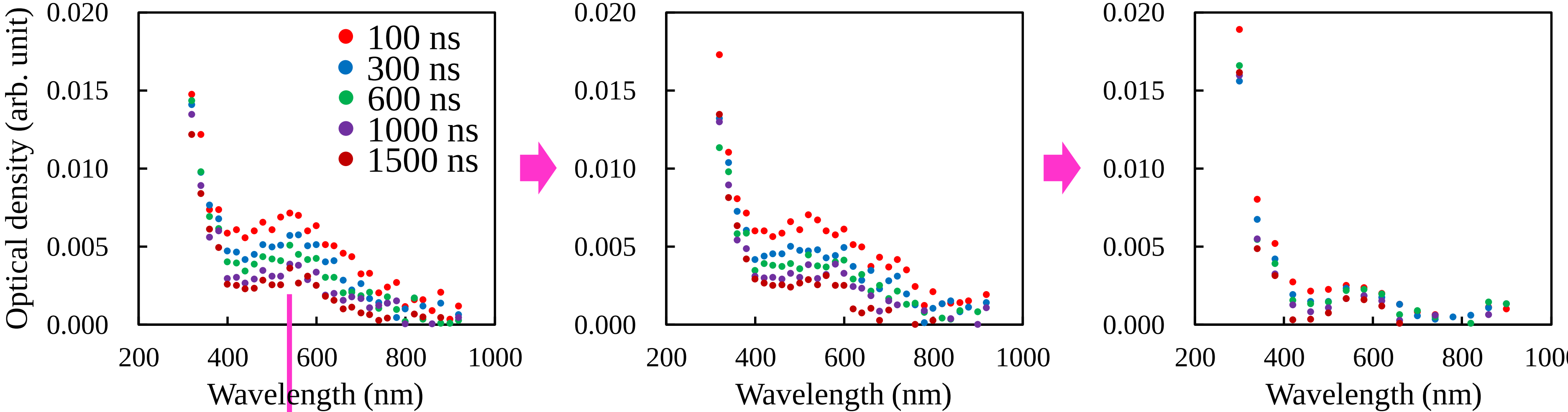


Fig. Transient absorption spectra obtained in the pulse radiolysis of IBA solution in water at 400 ns after an electron pulse.



Reaction of ligands with holes



0.1 M MAA in CH_2Cl_2 | +0.1M ethanol | +1M ethanol

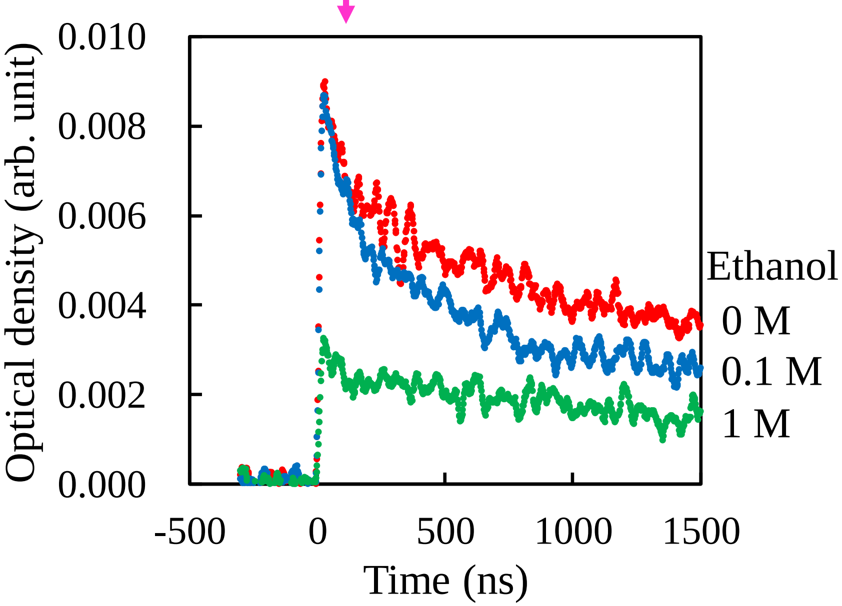
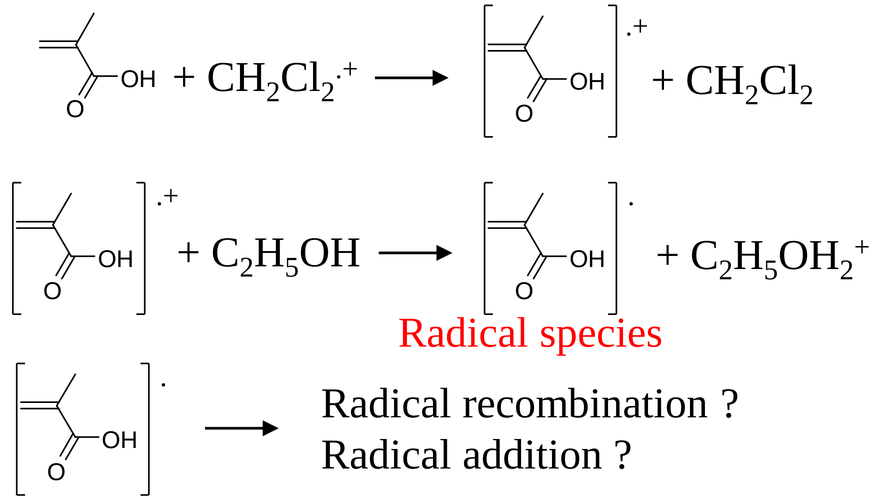
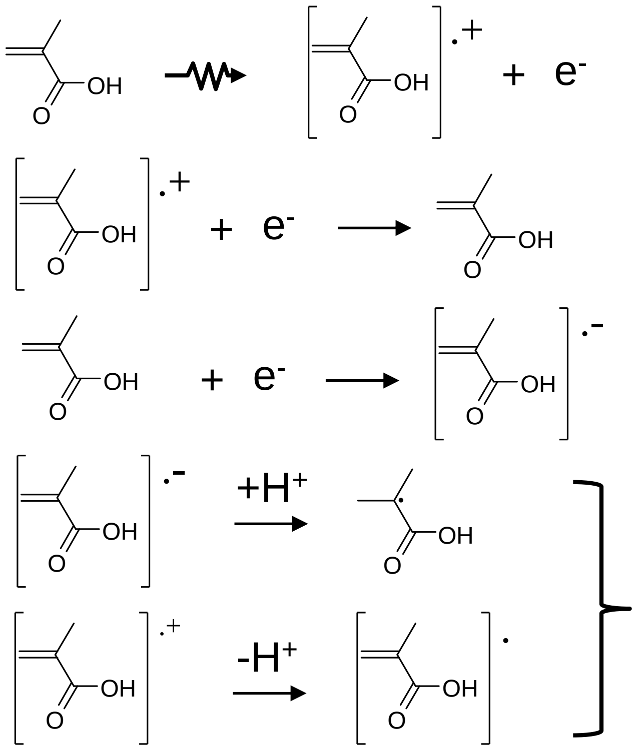


Fig. Kinetic traces of intermediates obtained in the pulse radiolysis 0.1 M MAA solution in CH_2Cl_2 with 0, 0.1, and 1M ethanol, monitored at 540 nm.



Possible reactions in real chemical system

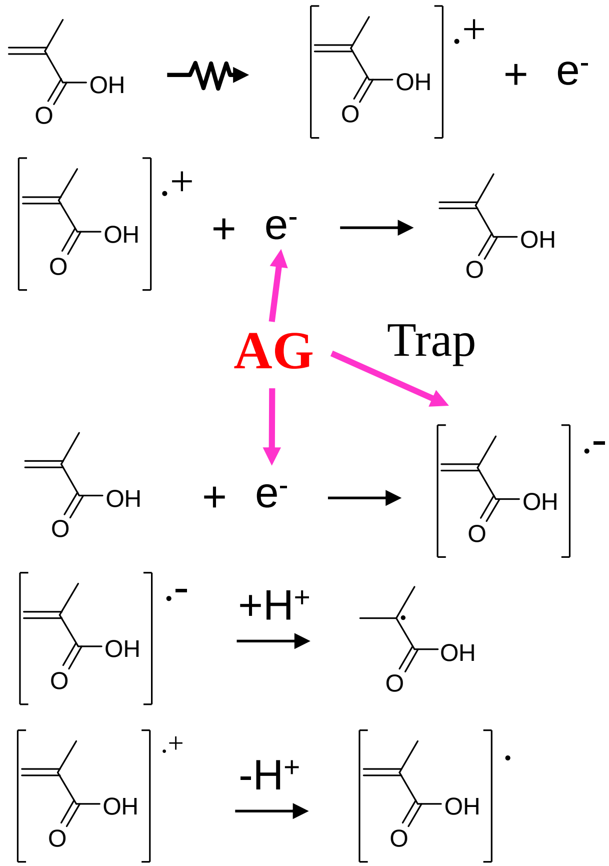


(including oxidation on ZrO_2 core surface)

(including reduction on ZrO_2 core surface)

Radical recombination ?
Radical addition ?

Effect of acid generator on chemical system

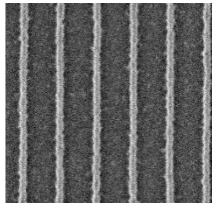


(including oxidation on NP surface)

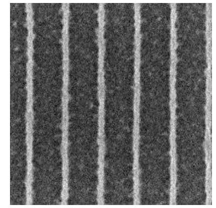
(including reduction on NP surface)

- ○ Suppression of MAA anion radical yield
- ○ Increase of MAA cation radical yield through the suppression of ion recombination
- ○ Suppression of electron migration
- ○ Generation of anions

Effect of acid generator on resist pattern

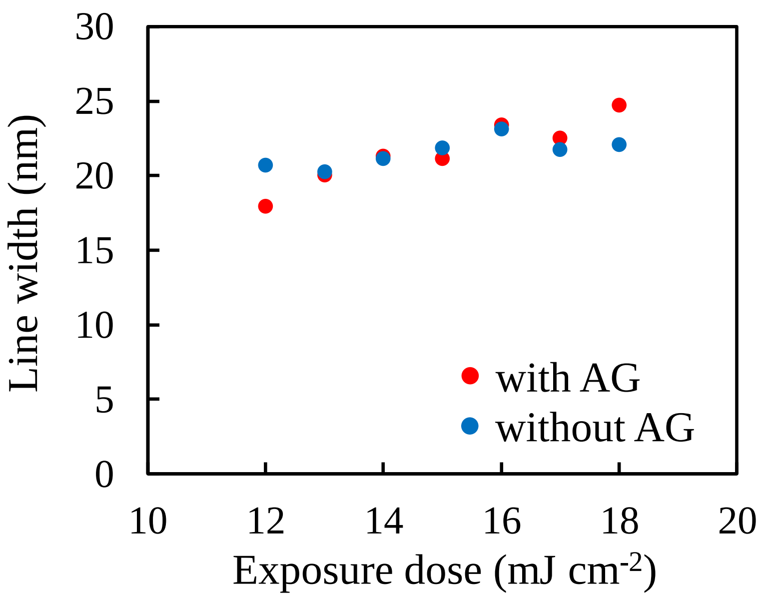


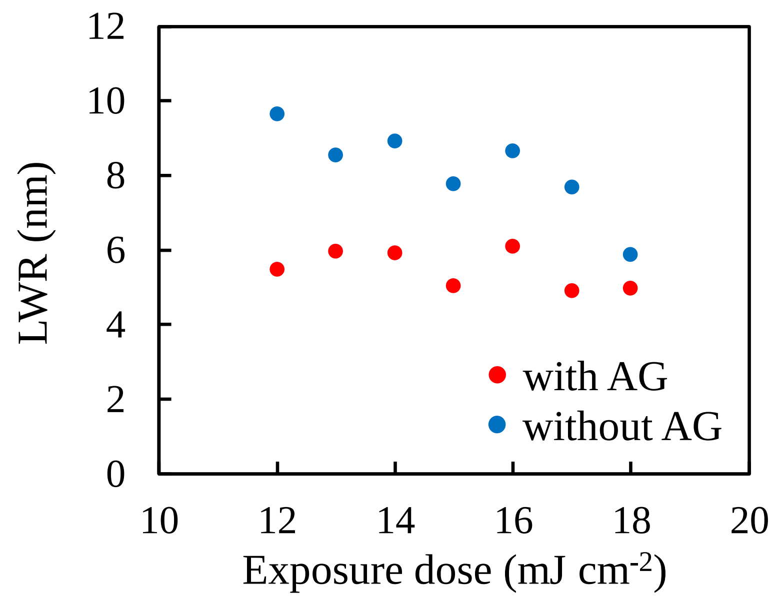
With AG



Without AG

1:5 L&S pattern
120 nm pitch
Developer: *n*-BA





Suppression of MAA anion radical yield
Increase of MAA cation radical yield

Balanced out

Suppression of electron migration

Both electron and hole contribute to pattern formation.

Summary

- ○ The radiation chemistry of ligands (MAA) was investigated using a pulse radiolysis method.
- ○ Both electrons and holes generated upon EUV exposure result in MAA radicals.
- ○ Both the reaction paths through MAA cation radicals and anion radicals are considered to lead to the insolubilization of the resist.
- ○ The acid generators suppressed LWR probably through capturing the thermalized electrons.

Acknowledgement

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