Future Prospect of Photosensitized Chemically Amplified Resist (PSCAR)

Seiichi Tagawa (Osaka University)

Nowadays **RLS trade-off and stochastic defects problems are important problems.**

Today' my talk is as follows:

1. Fundamental concepts of EUV CAR and PSCAR

2. Future Prospects of PSCAR

IEUVI Resist TWG meeting, February 23rd 2020 San Jose McEnery Convention Center

Talk today: Fundamental Concepts of CAR and PSCAR EUV lithography and Future Prospects of PSCAR

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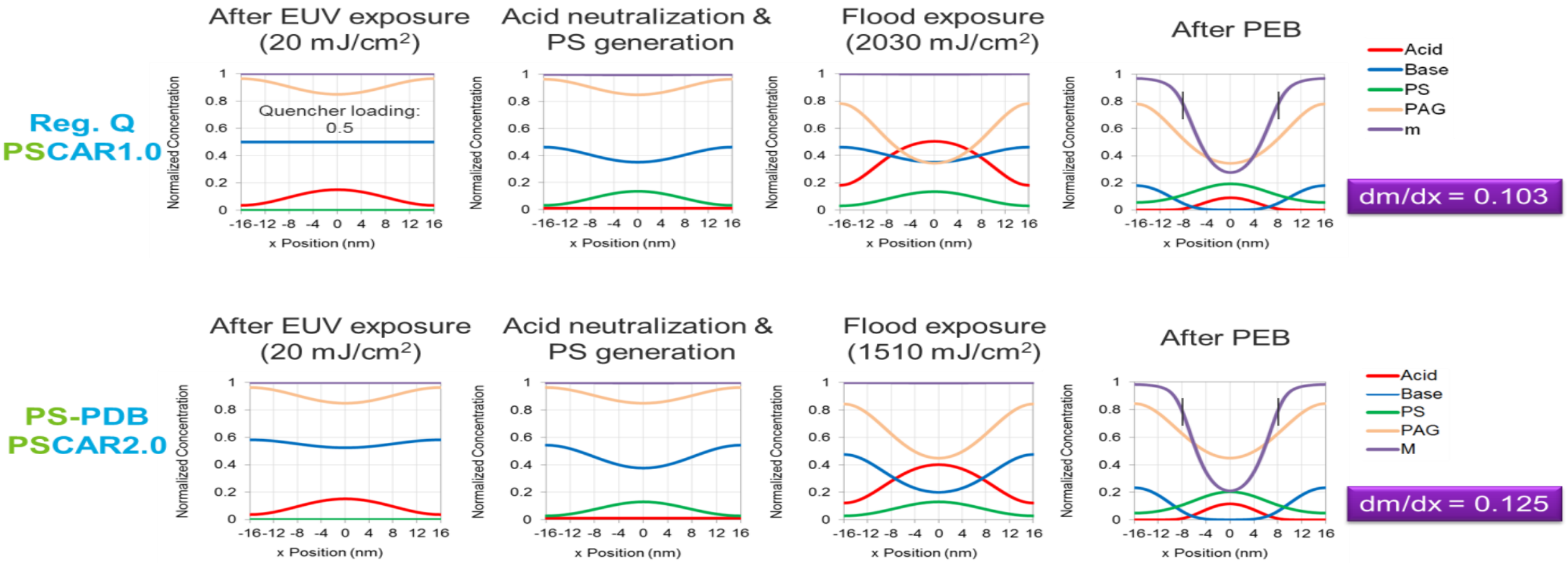
Today' my talk is as follows.

1. Fundamental concepts of EUV CAR and PSCAR
2. **Future Prospects of PSCAR**

Comparison of PSCAR 1.0 with PSCAR2.0 (Nagahara et al.,SPIE Advanced Litjography 2017)



In this SPIE Advanced Litjography 2020, Advances in Patterning Processes, Tuesday 10:30, Nagahara presents recent progress of PSCAR in industries.

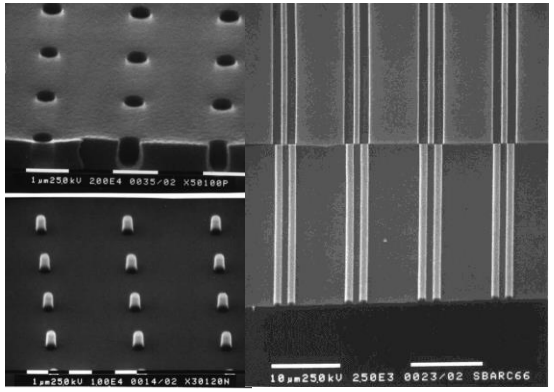
Step to PSCAR: Sensitivity Enhancement of CAR

- 1982 CAR:C.G.Willson, H.Ito and Fréchet
- 1984 Y.Tabata, S.Tagawa, M.Washio: EB Resist (CMS) reaction and HCl formation mechanisms were made clear by picosecond pulse radiolysis, such as geminate ion recombination, dissociative electron attachment, hole transfer.
- 1992 T.Kozawa, S.Tagawa et al: EB CAR resist reaction mechanisms were cleared by picosecond pulse radiolysis, geminate ion recombination, dissociative electron attachment, proton transfer
- 2000 S.Tagawa, S.Nagahara et al. : Differences between reaction mechanism of EB and KrF CAR were made clearly.
- 2004 S.Tagawa, *1st European Workshop on Resist Limitations,Erlangen, 14 December, 2004 and then Co-work with Intel (2005-2008)*
- 2005 Gallatin Gallatin: Importance of initial acid distribution for RLS trade-off were made clearly.
- 2008 Todd (Intel)' report: RLS trade-off
- 2010 Kozawa and Tagawa: Review of Radiation Chemistry of CAR
- 2009 Acid amplification:Arimitsu, Kudo, Ichimura(1998) et al. , Kruger, Brainard et al: paper of Acid amplification, K. Enomoto, Arimitsu et al (2012)
- 2013 PSCAR

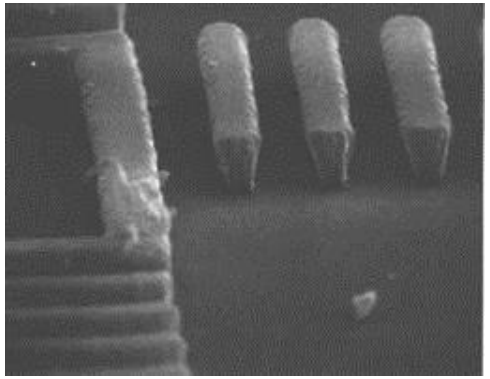
Chemical Amplification Resists

The Beginning (1)

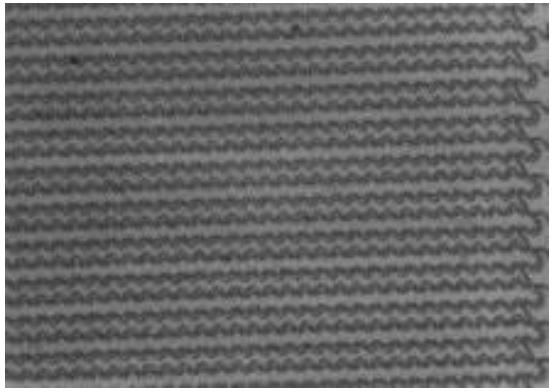
When Hiroshi Ito joined IBM in 1980, high sensitivity of deep UV resists was required because of very weak intensity of deep UV exposure source. He began working on several projects under C.G.Willson. They proposed three systems: an acid-catalyzed polarity change, cationic polymerization and depolymerization. As the three systems were characterized with a gain mechanism, they decided to call these resist systems "chemical amplification resists."



Deprotection of t-BOC



Crosslinking of SU-8



Depolymerization

Reaction mechanisms of EUV and photo resists

・EUV resists（Main process） Ionization channel

RH: polymer

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

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

_S. Tagawa, et.al. *SPIE* 3999 (2000) 204

・Photoresists（Main process） Excitation channel

RH:Polymer

$$Ph_2S^{\cdot+} + Ph^{\cdot} + X^- \xrightarrow[\text{cage-escaped}]{RH:} Ph_2S$$

Homolysis

$$(Ph_3S^+X^-)^* \rightarrow Ph_2S^{\cdot+} + Ph^{\cdot} + X^-$$

in-cage Reconbination

$$(Ph_3S^+X^-)^* \rightarrow Ph_2S + Ph^+ + X^-$$

Heterolysis

in-cage

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

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

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

X

$$Ph_2S + Ph^+ + X^- \xrightarrow[\text{cage-escaped}]{RH} Ph_2S + PhR + H^+X^-$$

1. Dissociative Electron Attachment
2. Geminate ion recombination
3. Proton Transfer (Hole Transfer)

Energy Absorption Process of EUV Resists

Intensity of EUV (I)

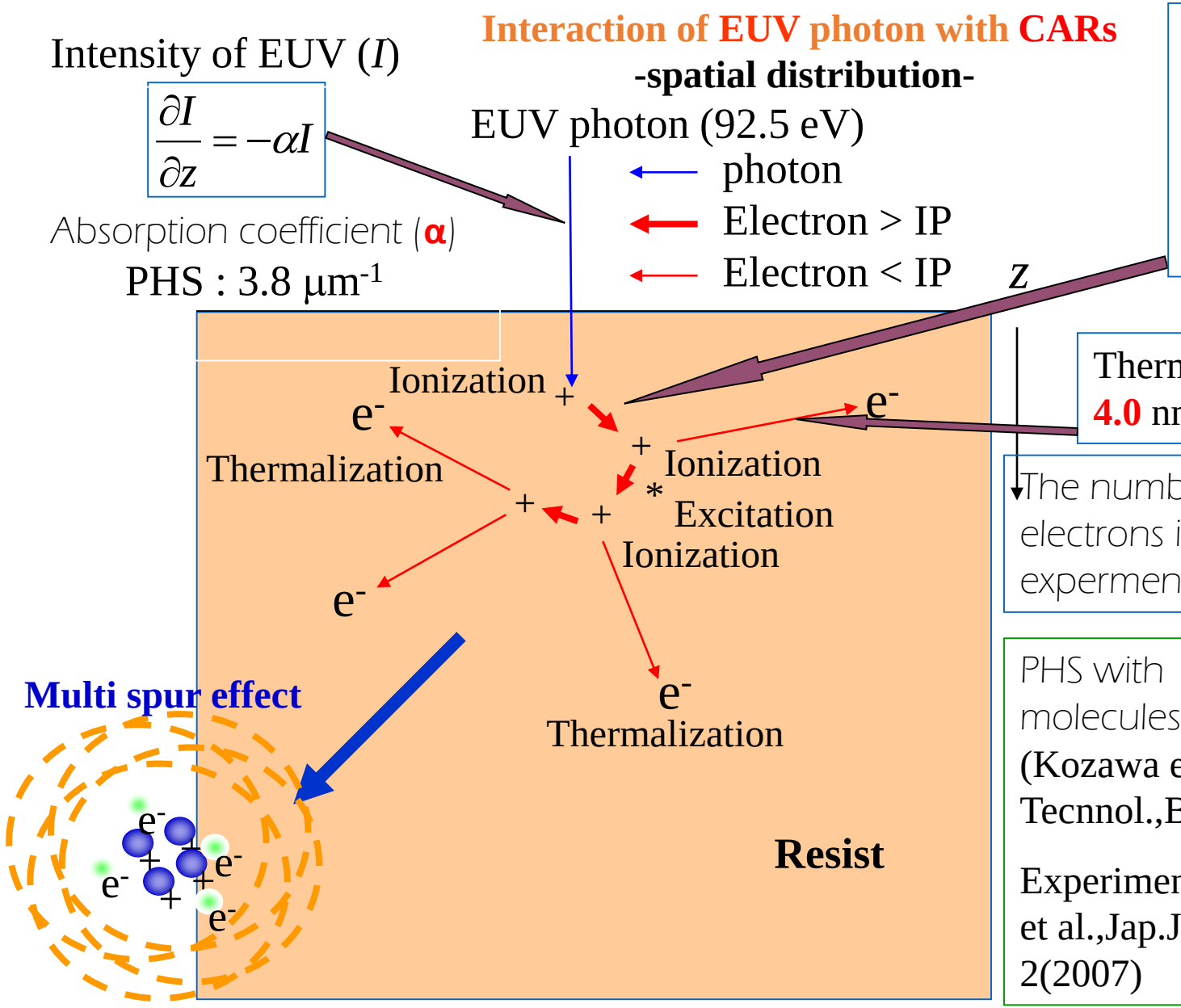
$$\frac{\partial I}{\partial z} = -\alpha I$$

Absorption coefficient (**α**)

PHS : 3.8 μm^{-1}

Interaction of EUV photon with CARs

-spatial distribution-



Inelastic mean free path

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

Thermalization Length

4.0 nm for PHS

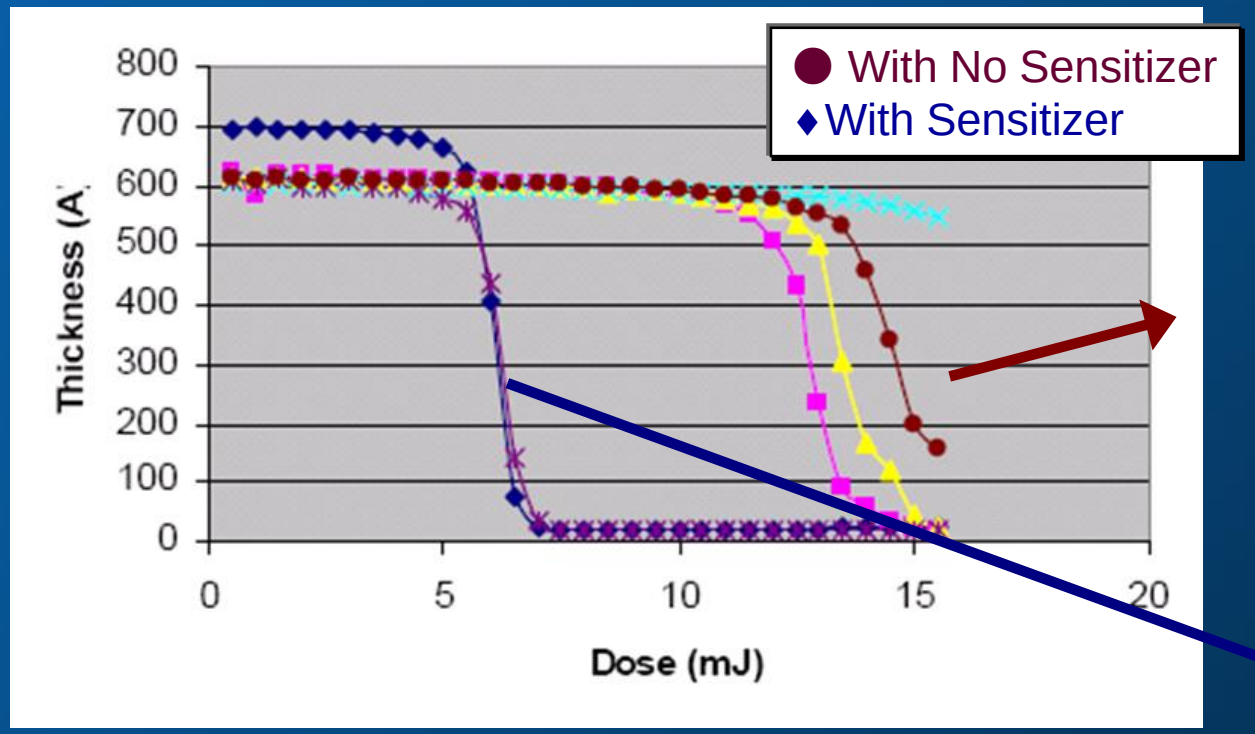
The number of secondary electrons is estimated expermentally. 4.2 for PHS

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

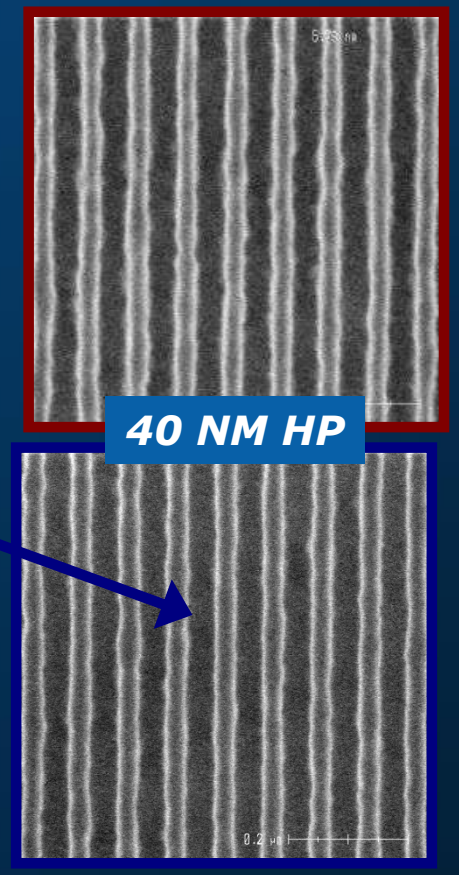
Experimental value: **2.5** (Hirose et al.,Jap.J.Appl.Phys,Part 2(2007)

EUV Mechanism[1] Provides RLS Gain?

[1]Kozawa, et al. JVSTB 25, 2481 (2007)



Resist A
S=27.5 mJ; L<5.5 nm



Resist B
S=14.0 mJ; L<5.0 nm

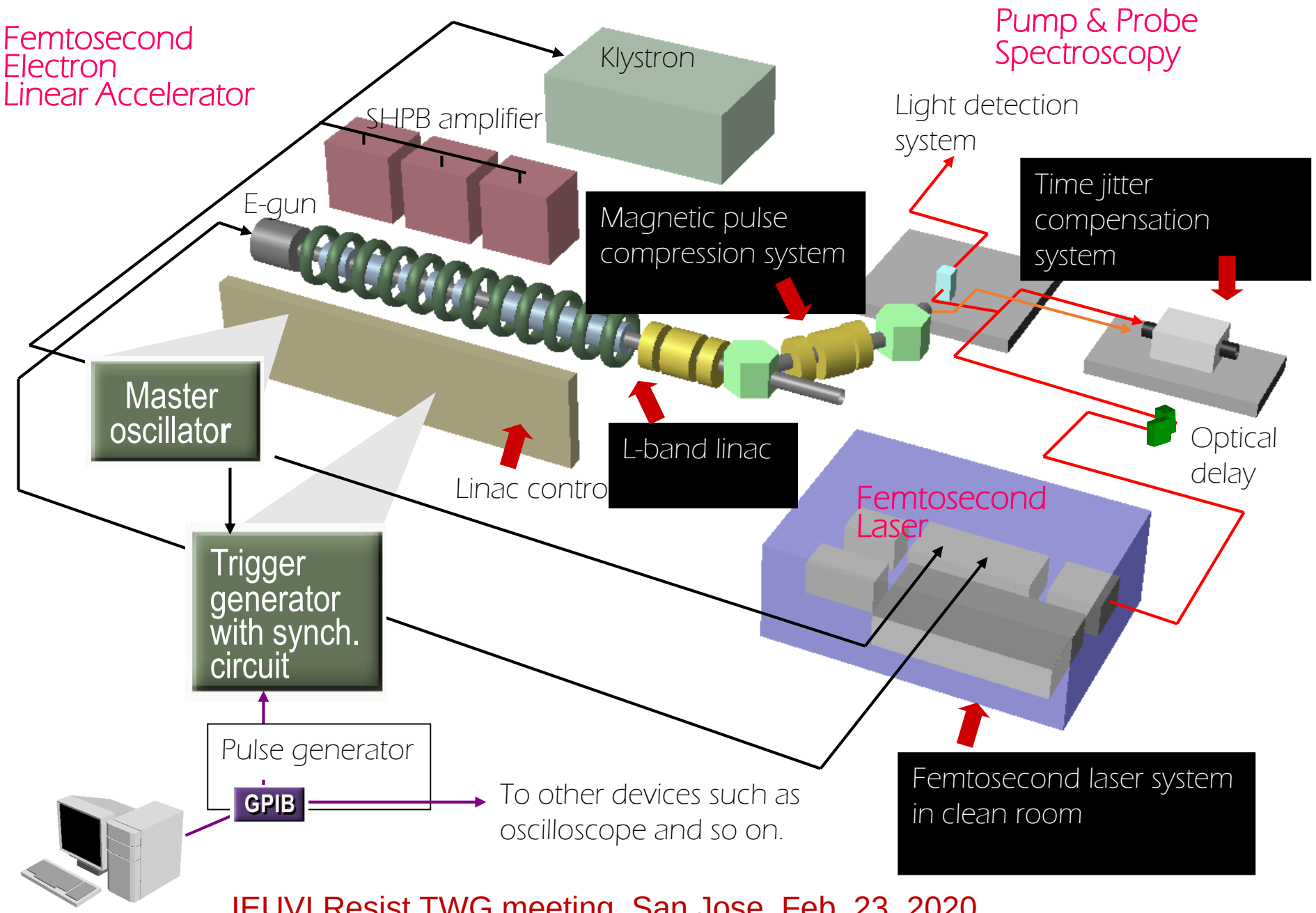
- **Resist Sensitivity Improved 30-50% via Addition of EUV Sensitizing Agents.**
- **No Loss In Resolution or Degradation in LWR**

Multiple Suppliers Achieving Similar Results in 1H'08

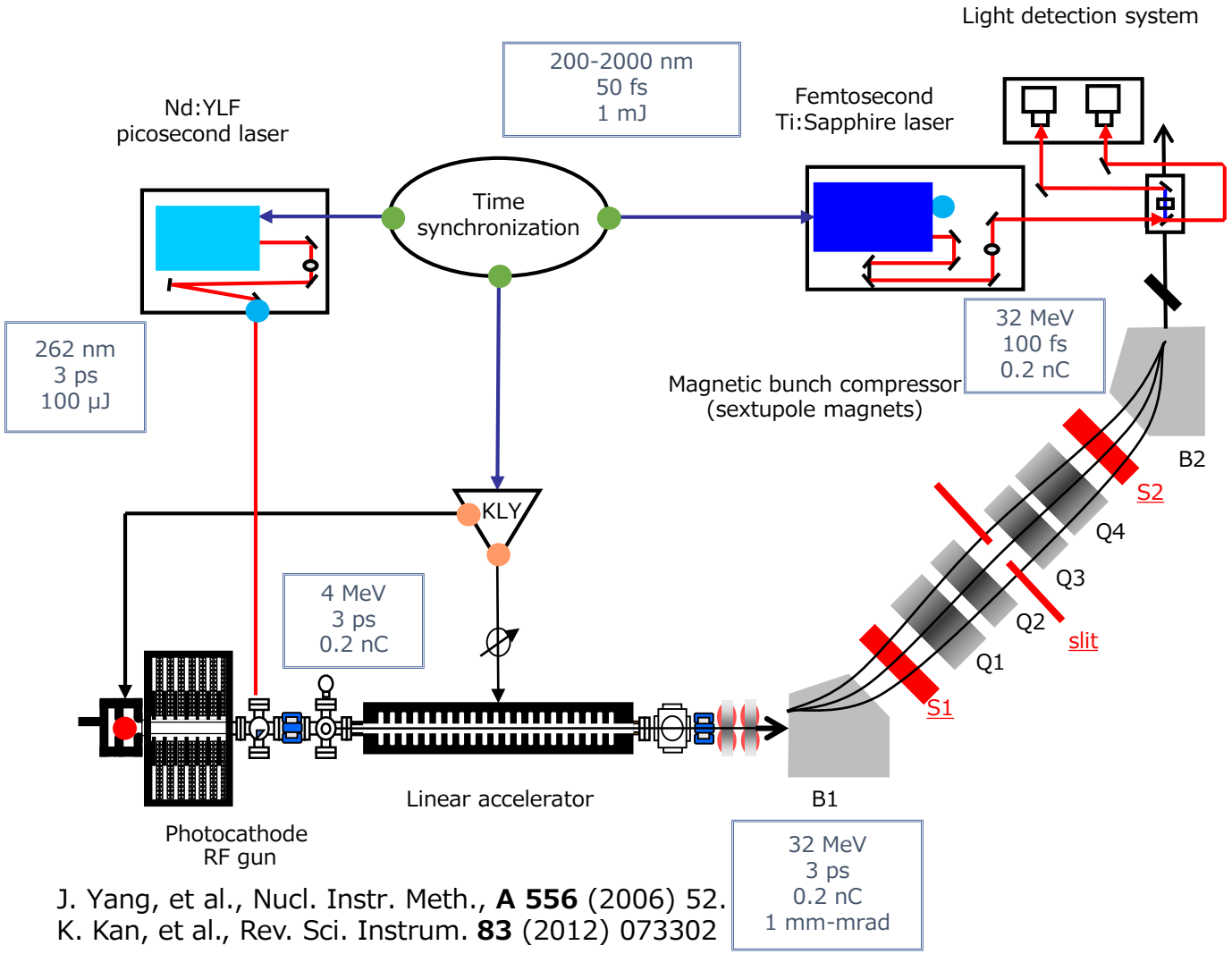
Todd R. Younkin, Components Research Technology Manufacturing Group, Intel Corporation (2008)

IEUVI Resist TWG meeting, San Jose, Feb, 23, 2020

Subpicosecond Pulse Radiolysis System

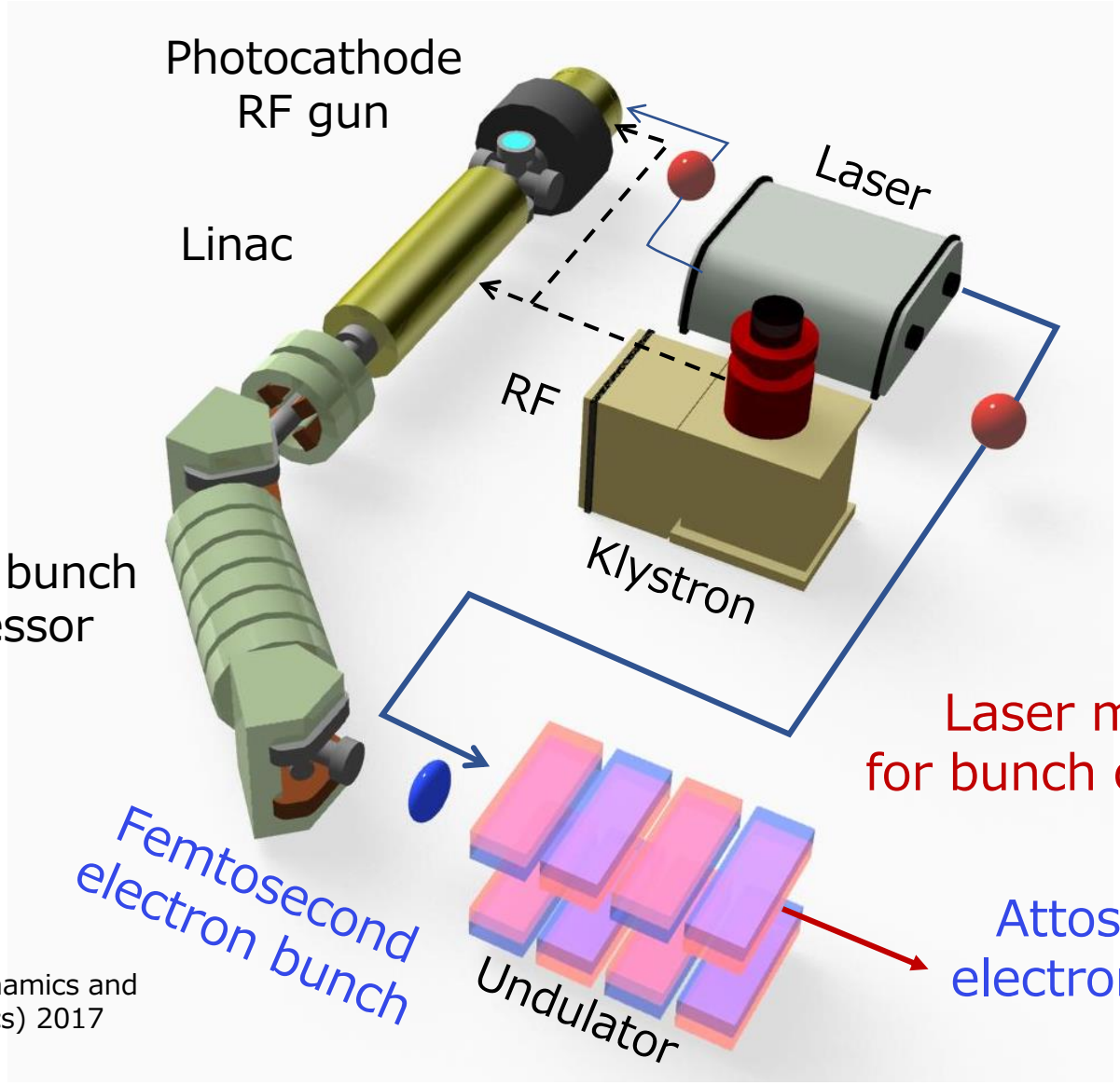


Femtosecond pulse radiolysis system @ISIR, Osaka Univ.



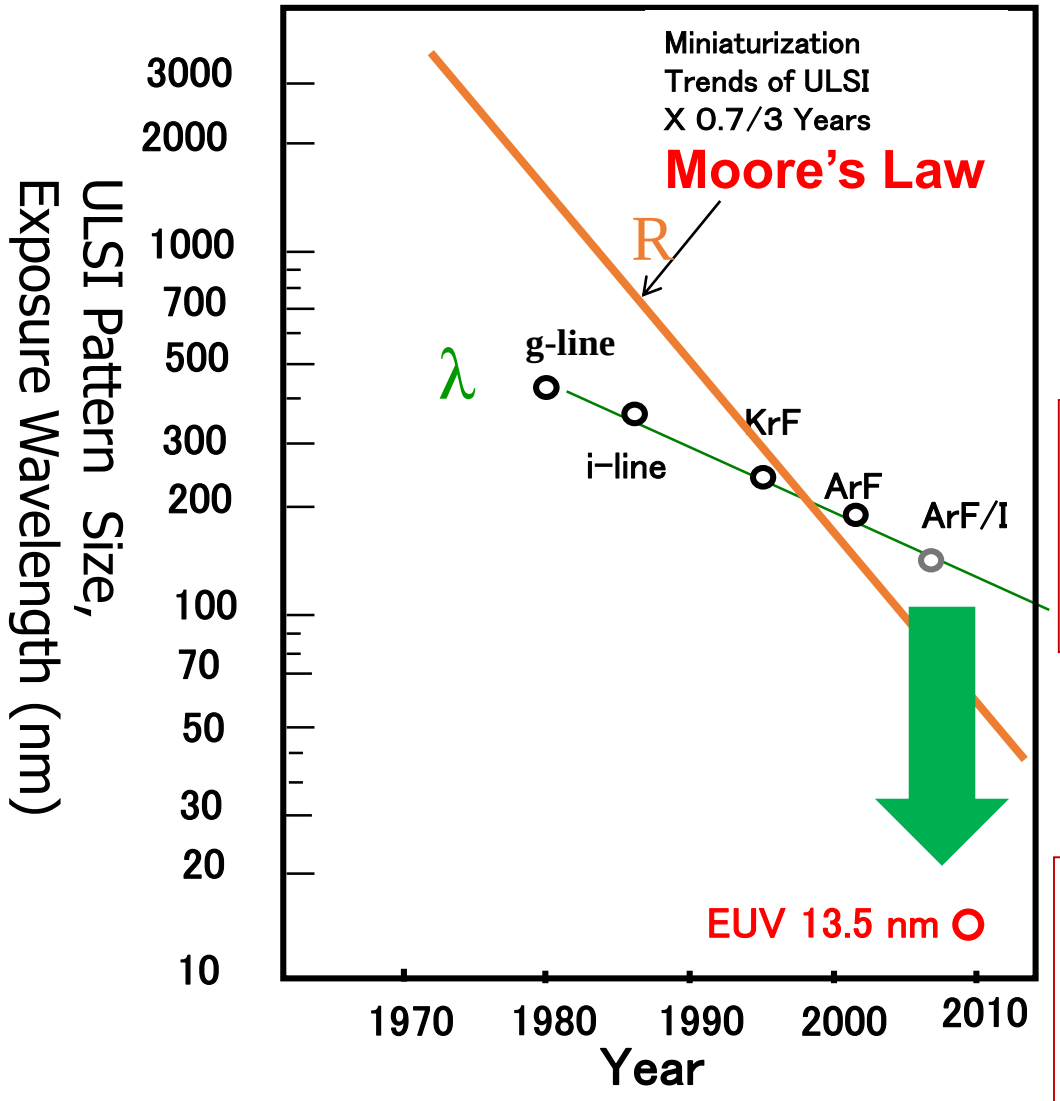
J. Yang, et al., Nucl. Instr. Meth., **A 556** (2006) 52.
K. Kan, et al., Rev. Sci. Instrum. **83** (2012) 073302

Attosecond pulse radiolysis (next plan)



K. Kan *et al.*, Proc. NOCE (Nonlinear dynamics and Collective Effects in particle beam physics) 2017

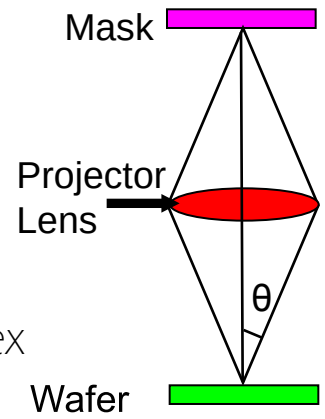
Miniaturization of ULSI and Exposure Wavelength Reduction Trends



$$R = k_1 \frac{\lambda}{NA}$$

NA=n・sinθ

n：Reflective index



R: resolution λ:exposure wavelength
k_1 : constant depending on resist materials and processes and exposure methods
NA: numerical aperture of optical system

Very Big Change from ArF to EUV Lithography

Only less than 2.3 times reduction from g-line to ArF (436 nm/193 nm) takes more than 20 years, but more than 14 times reduction (193 nm/ 13.5 nm) occurs from ArF to EUV.

PSCAR process flow to break RLS tradeoff relationship

Coating and PAB
Resist Coating

EUV pattern exposure
Acid and photosensitizer generation

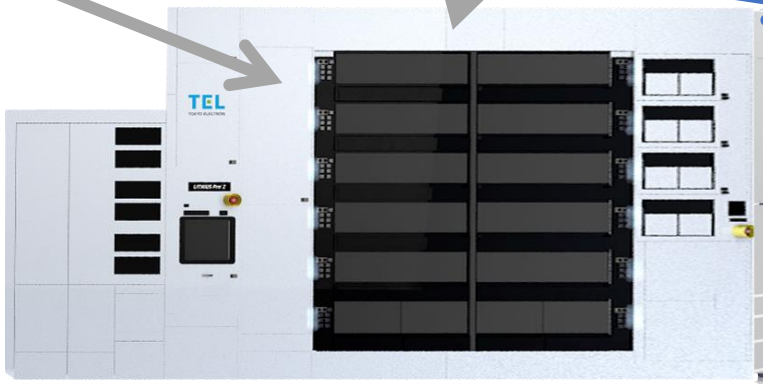
UV flood exposure
Additional acid generation by photosensitization

PEB
Resist polarity change reaction (deprotection etc.)

Development
High sensitivity& high resolution pattern formation

PSCAR™

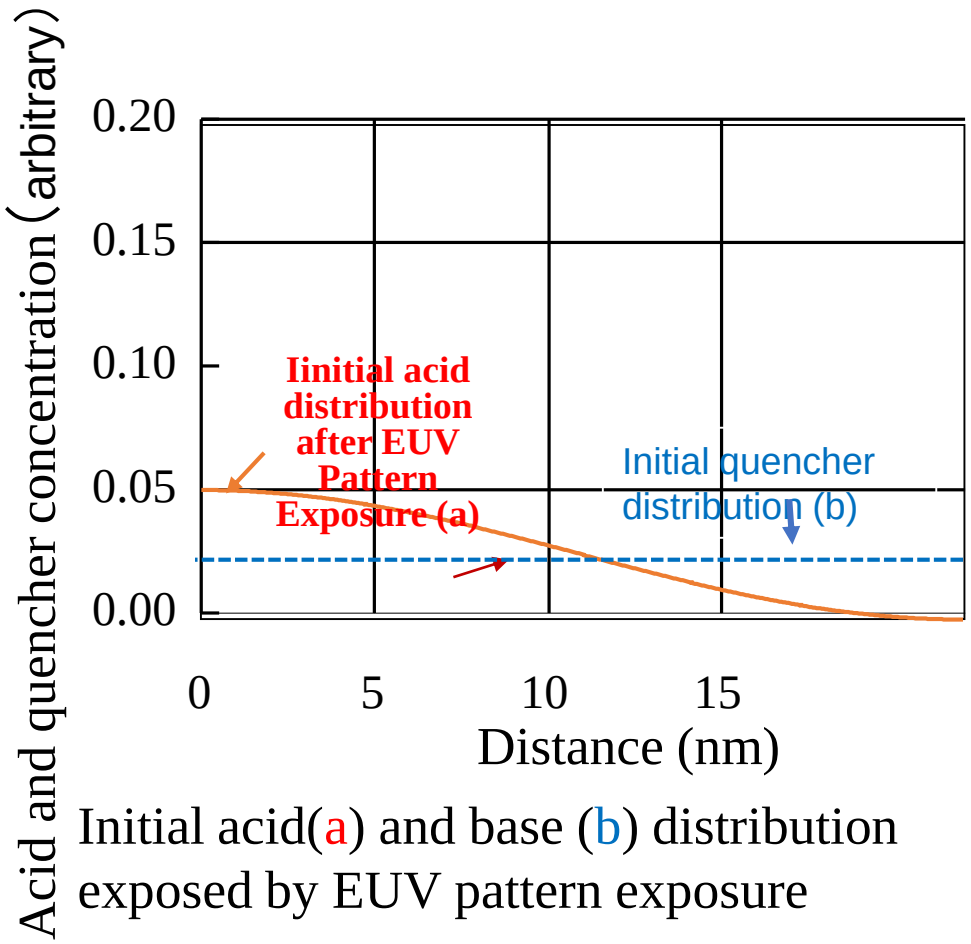
Photo-Sensitized Chemically Amplified Resist™



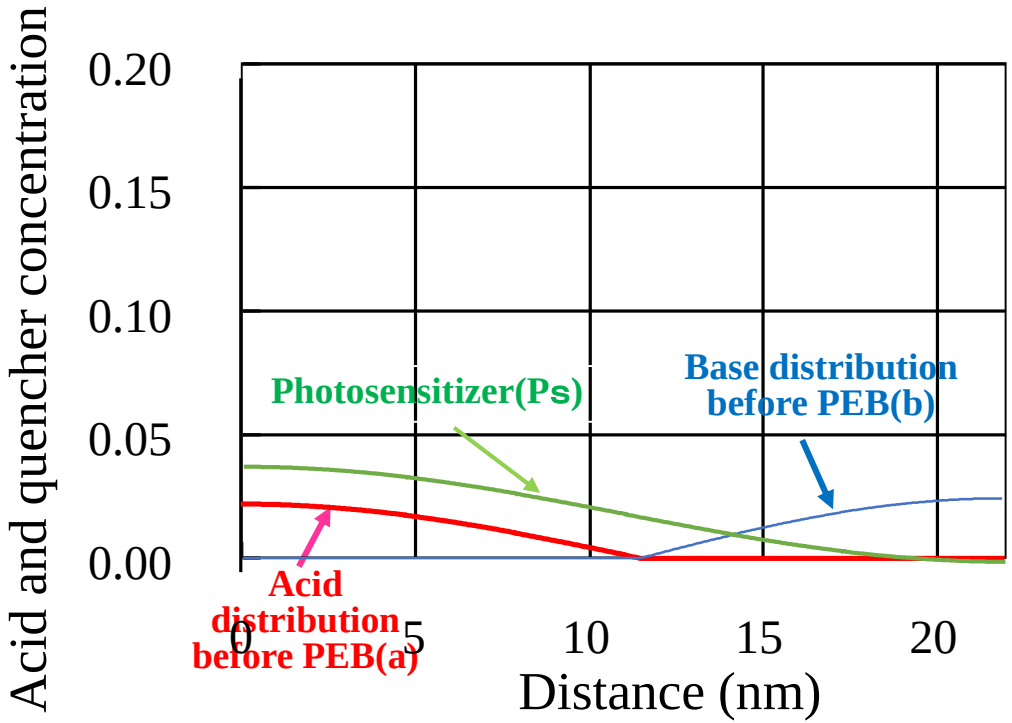
TEL CLEAN TRACK™

ASML NXE EUV exposure tool

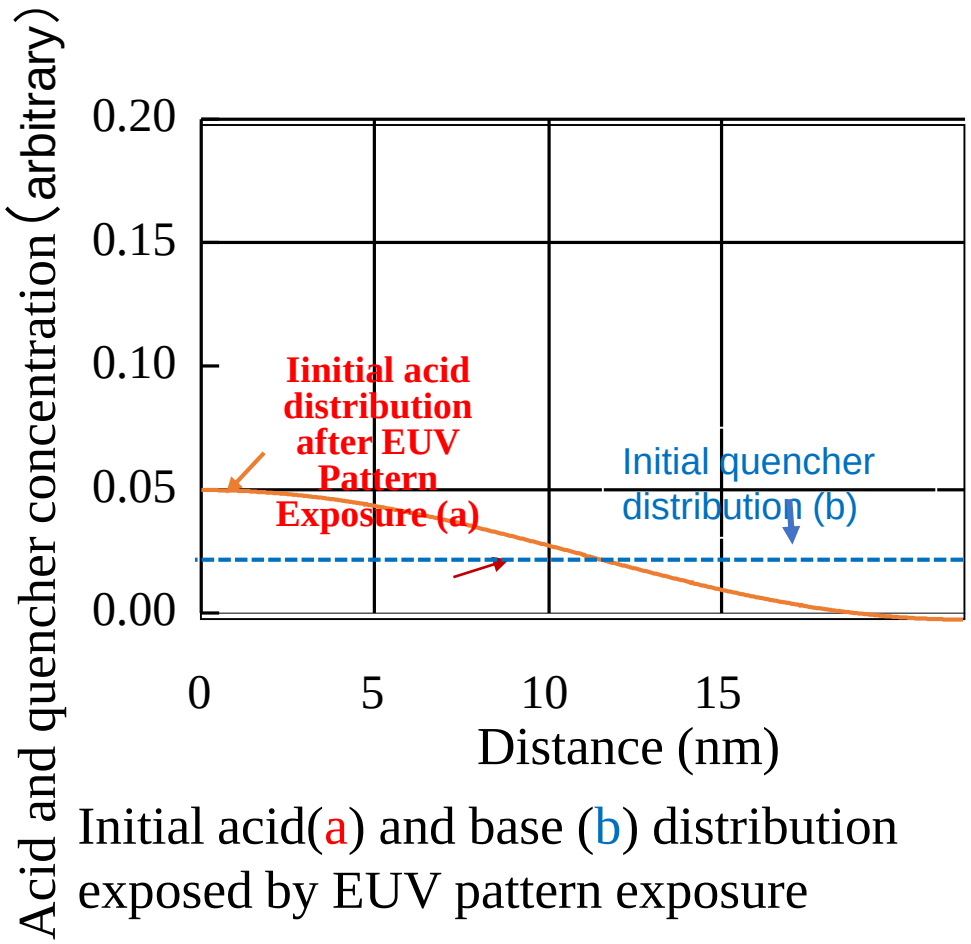
PSCAR material and UV flood exposure module are new development items



Initial acid(a) and base (b) distribution exposed by EUV pattern exposure



When photosensitizer generation is much faster than acid and base neutralization, acid (a), quencher (b) and photosensitizer(PS) distributions are shown.



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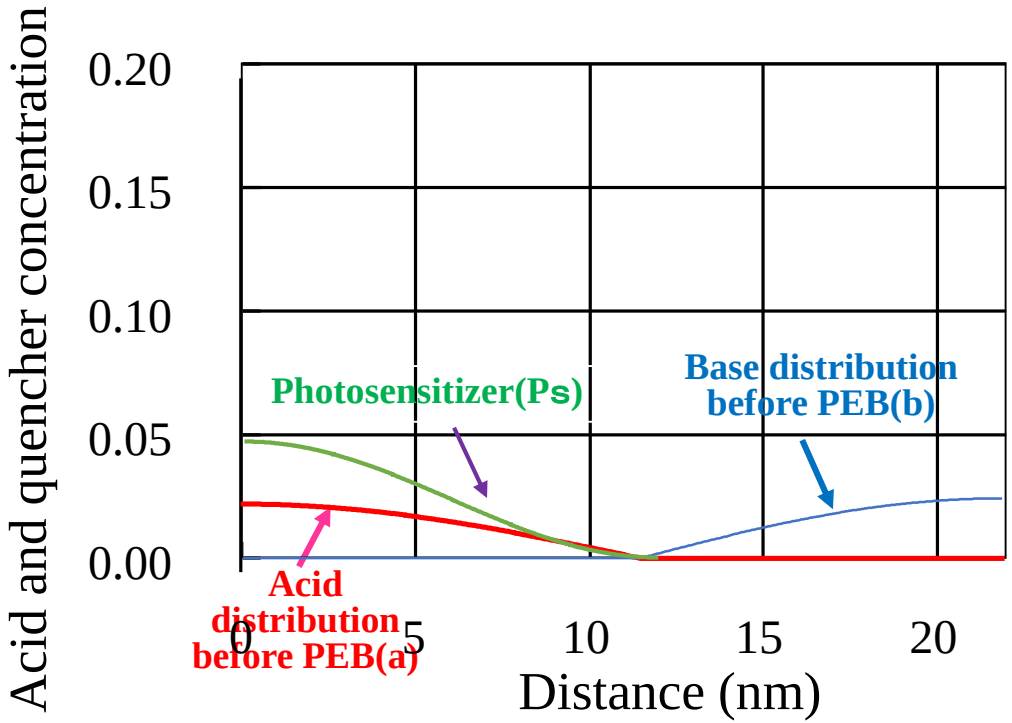
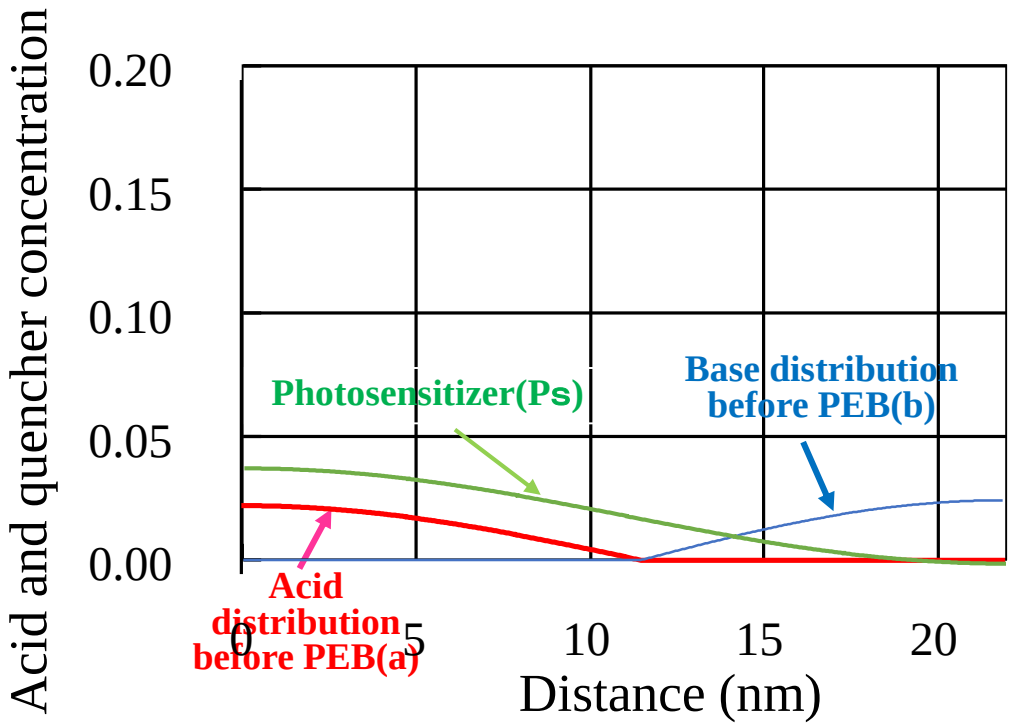


When photosensitizer generation is much slower than acid and base neutralization, acid (a), quencher (b) and photosensitizer(PS) distributions are shown.



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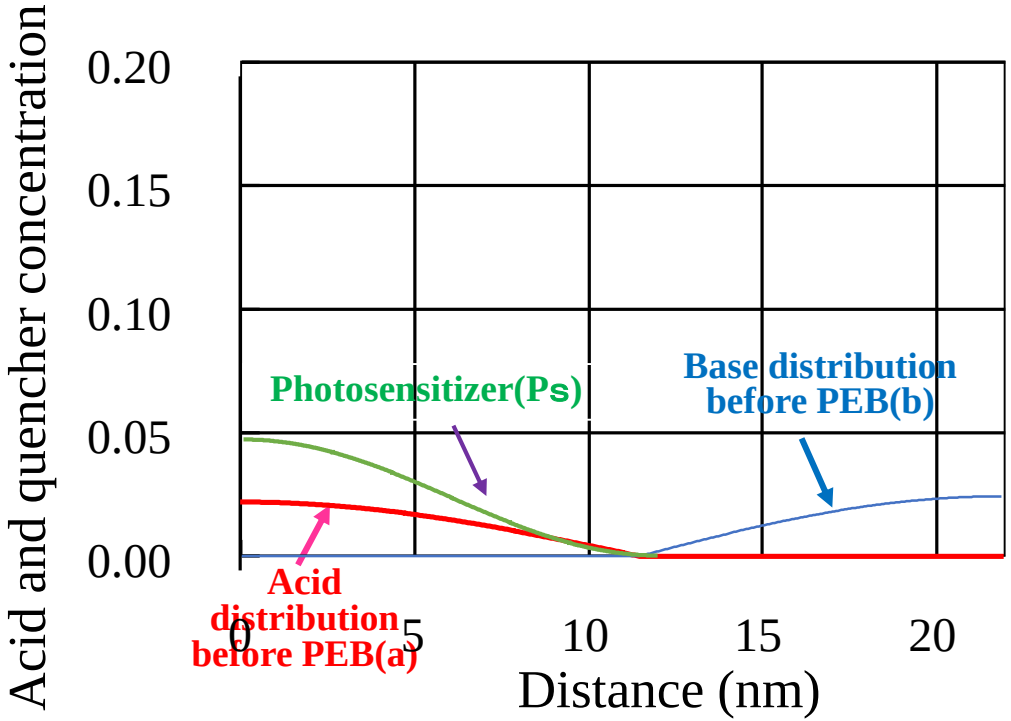

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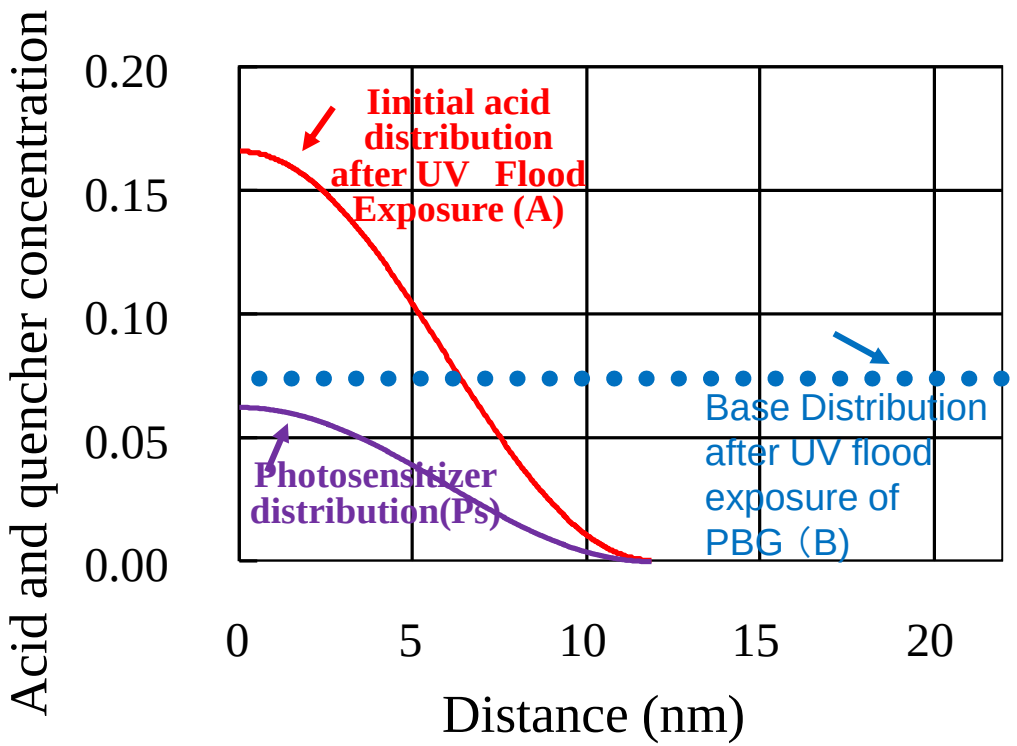
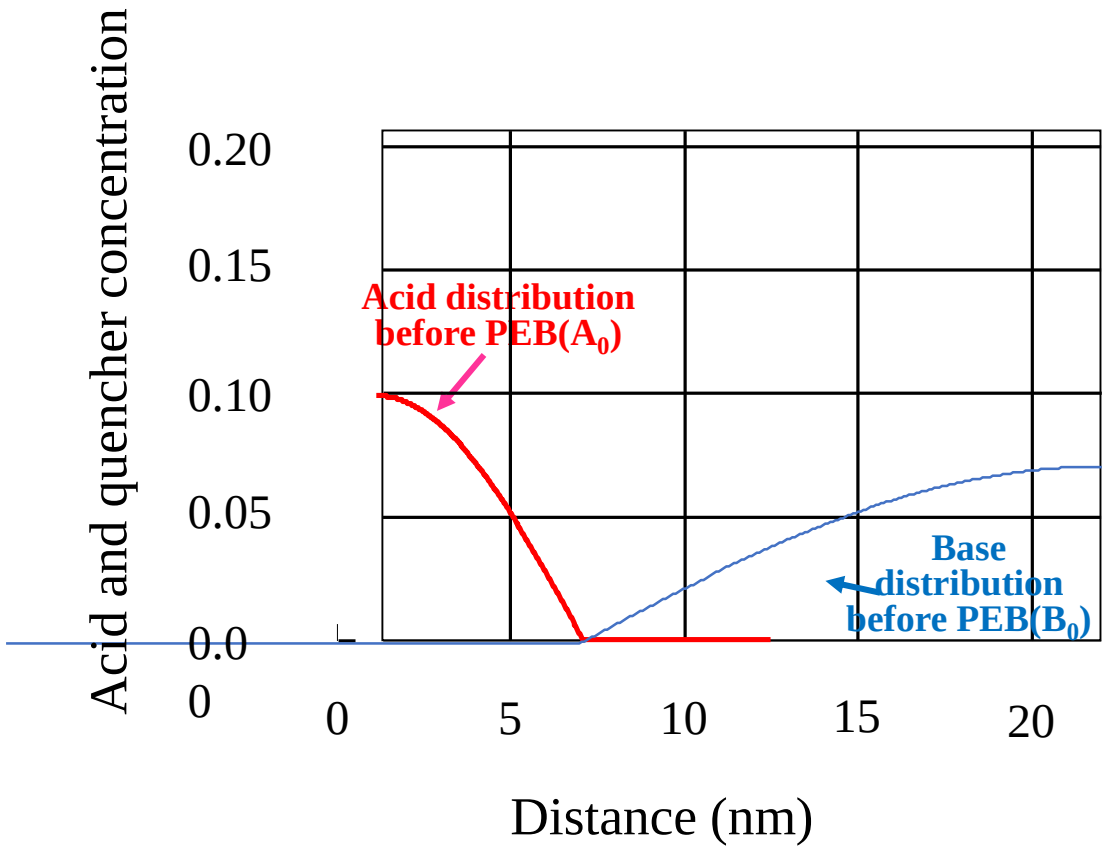


Acid (A) and quencher concentration(B) of resist containing PBG after UV flood exposure



Acid (A) and quencher concentration(B) of resist containing PBG after UV flood exposure before PEB

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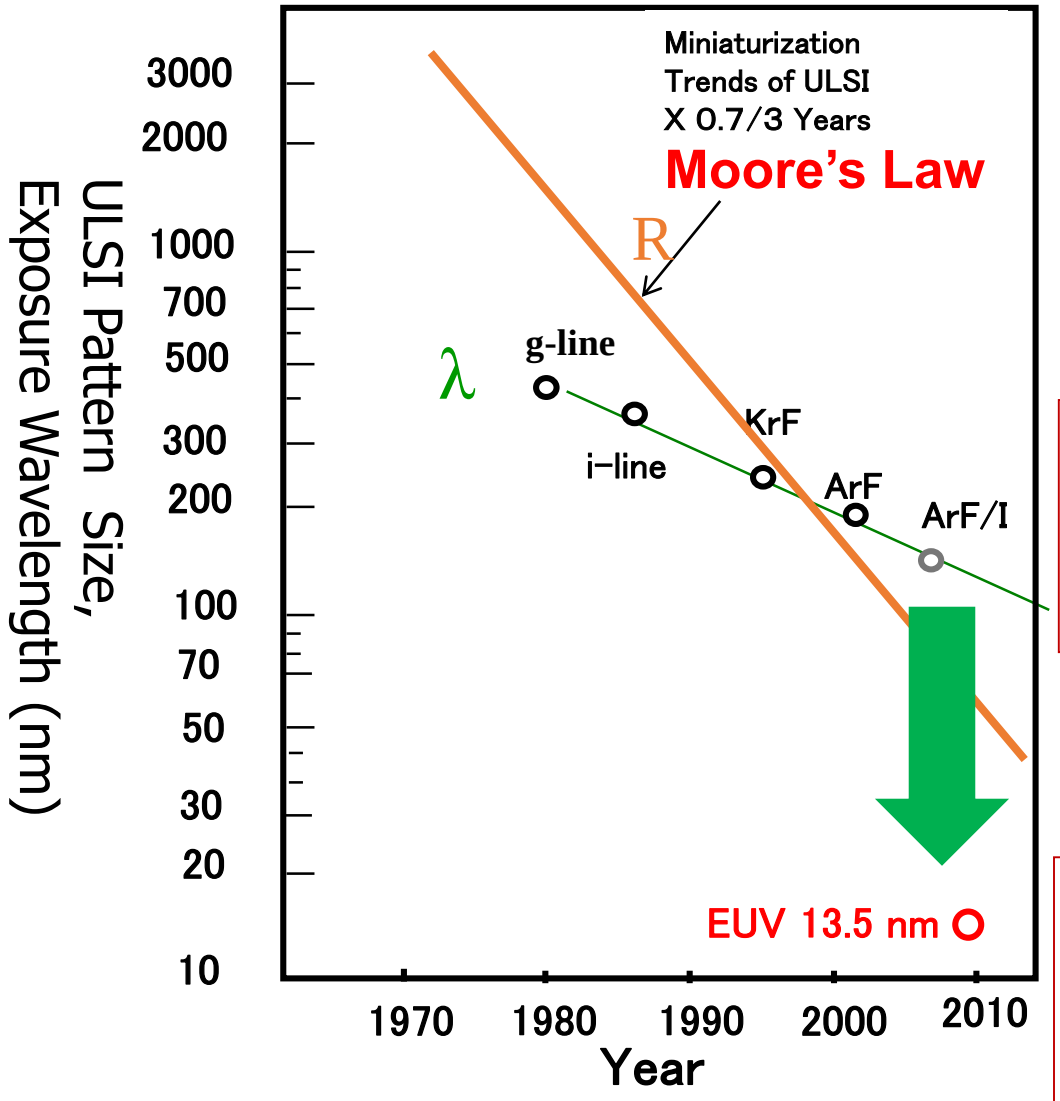

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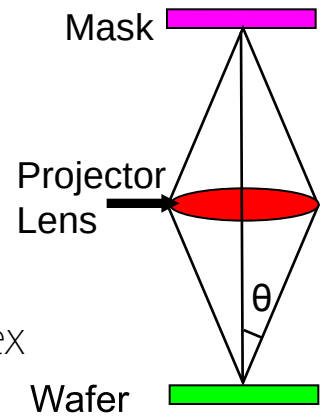

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Conclusion

- The new PSCAR processes can produce much higher concentration of photosensitizer (PS) than other PSCAR because of low quencher concentration during EUV exposure. It is good for stochastic problems.
- Higher PS can reduce flood exposure dose. The lower flood exposure dose is good for UV flood exposure side reaction problems. It is good for random noise problems.
- The new PSCAR processes can keep constant pattern resolution even for higher dose based on the control of the ratio of acid yields to quencher yields. EUV pattern exposure determine the pattern size and the new PSCAR flood exposure process getting high sensitivity without losing resolution. The new PSCAR has the possibility ofovercoming or reducming the stochastics problems such as missing and kissing contact holes and micro-bridge and line braking of line/space.

Acknowledgments

We would like to acknowledge members of collaboration members of PSCAR process.

Thank you for your kind attention.