Fundamental Aspect of Photosensitized Chemically Amplified Resist

How to overcome RLS trade-off

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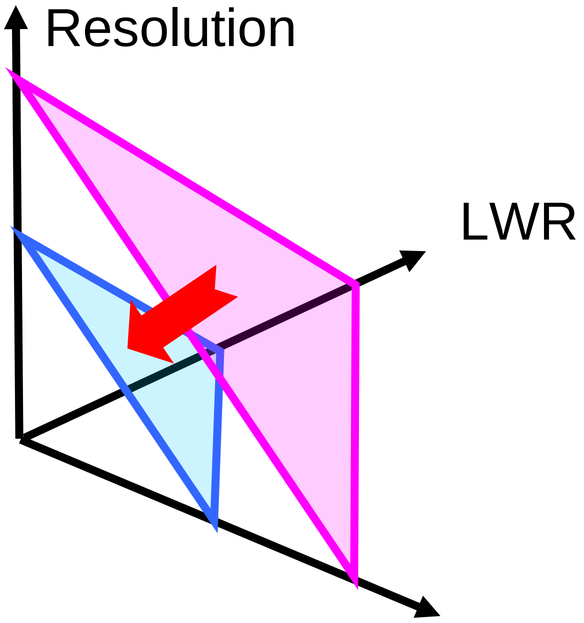
2016 International Workshop on EUV Lithography

Critical Problems of Next Generation EUV Lithography

1. **The most important critical issue of EUV lithography is the weak intensity of EUV source.**
2. **The resist sensitivity and the exposure light intensity are complimentary. Therefore high sensitization of EUV resists is required.**
3. **However, dramatic enhancement of resist sensitivity is widely confirmed to be difficult due to RLS trade-off problem.**



Solution of RLS Trade-off Problem

Simulations: *G.M. Gallatin, Proc. SPIE (2005)*, (no fundamental differences in simulations among ArF, EB and EUV resists after latent acid image formation.)

① Exposure (Tool)

② Interaction of EUV with resists

③ Accumulated energy profiel

④ Acid generation

⑤ Latent acid image

⑥ Acid diffusion, deprotection reaction

⑦ Acid catalyzed image (Latent image after PEB)

⑧ Development

⑨ Resist pattern formation

⑩10Other Treatments: Vapor smoothing, Hardbake, Ectching, Ozonation, etc.

Resist Pattern Formation Processes of EUV CARs

A review paper: Kozawa and Tagawa, (2010)

New Process: Reconsideration of acid generation mechanisms ④

Radiation chemistry ➡ Radiation chemistry + Photochemistry

New process: PSCAR

A very new high resist sensitization process by the combination lithography of EUV or EB pattern exposure with UV flood exposure of *Photosensitized Chemically Amplified Resist*™ (PSCAR™) was proposed at Osaka University in 2013.

(S.Tagawa et al., J.Photoplm. Sci. Tech. 26, 825 (2013)

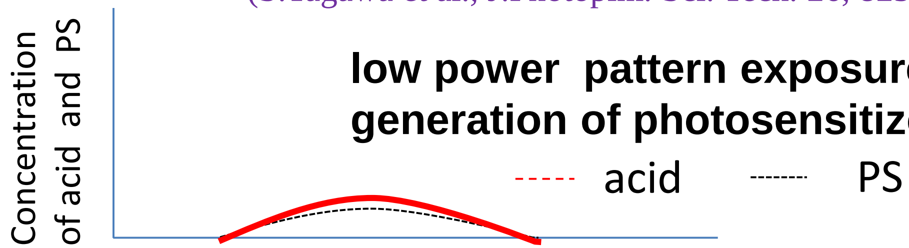
1. The first EUV pattern exposure produces photosensitizers (PSs).
2. Resist has no absorption band at the second flood exposure light wavelength. Therefore, no reaction of resist occurs by only the second flood exposure.
3. Only PSs have absorption bands at the second flood exposure wavelength.

New Process: Combination of radiation chemistry with photochemistry

(S.Tagawa et al., J.Photoplm. Sci. Tech. 26, 825 (2013)

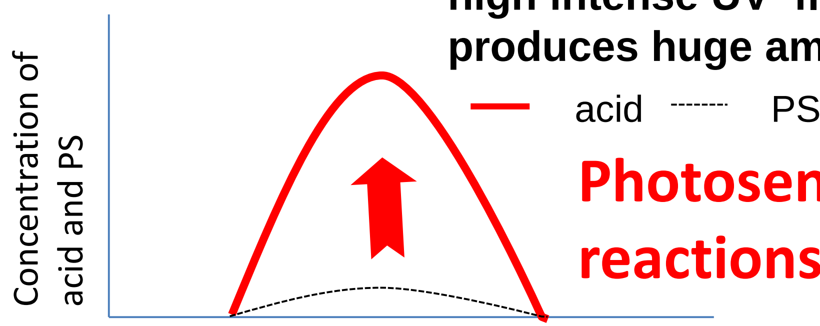
(1st exposure)

low power pattern exposure→
generation of photosensitizer (PS) and acid



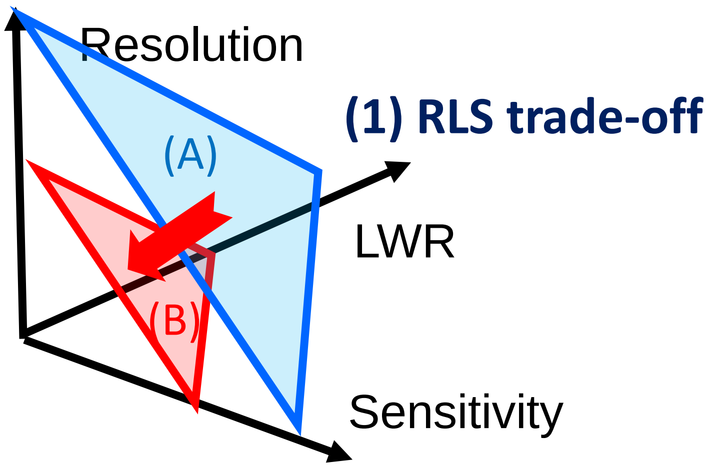
high intense UV flood exposure
produces huge amount of acid

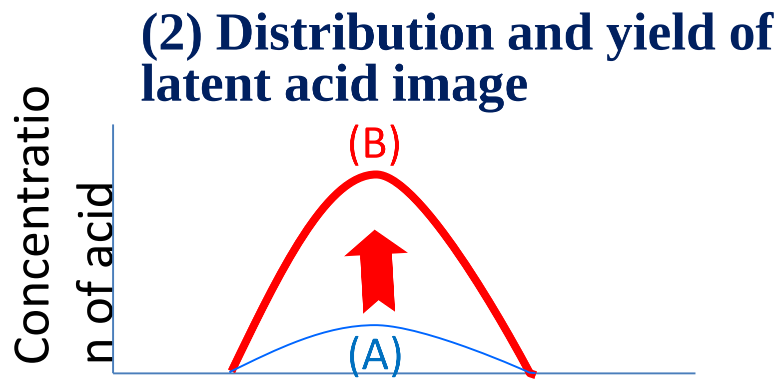
(2nd exposure)



Photosensitized acid generation reactions at room temperature

Breakthrough of RLS trade-off





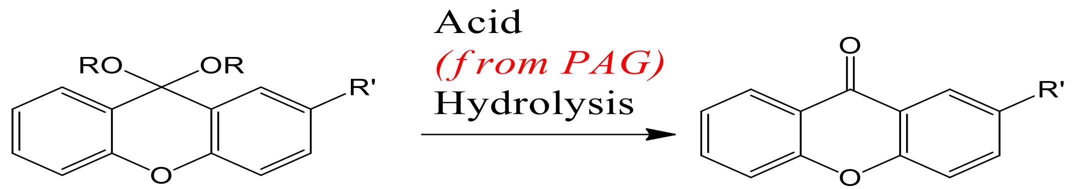
Schematic drawing of (1) RLS trade-off (2) initial distributions and yields of acid. If initial acid yield increases from (A) to (B) with the same distribution, RLS trade-off is improved from (A) to (B). (S. Tagawa, SPIE Newsroom, 13 March 2014)

The higher concentration of quencher can be used at same resist sensitivity. Then, the higher chemical gradient can be obtained.

fluctuation of sensitivity enhancement of PSCAR containing PP-2

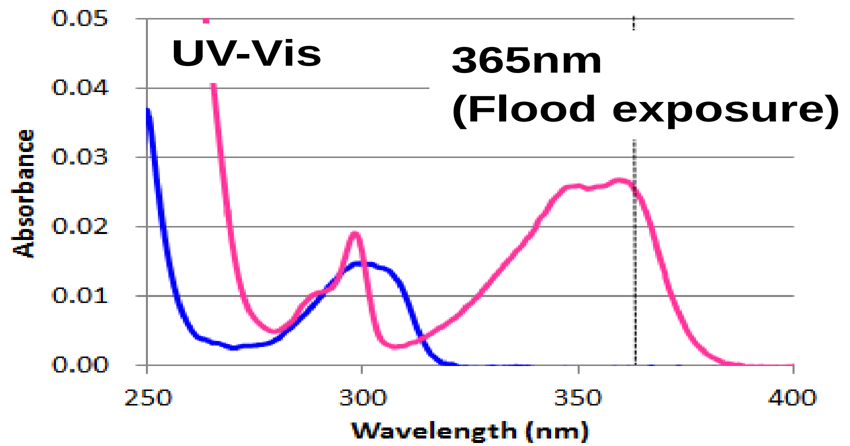
- In SPIE Advanced Lithography 2016, Osaka University, TEL Group, JSR, PSI, ASML reported 5 oral presentations on PSCAR. PSCAR enabled good with various CAR systems, especially PSCAR containing PP-2 made by JSR enabled the highest UV flood sensitization for 30 nm dense CH (contact hole) patterning by EBL at Osaka University.
- Three papers on EUV-IL at PSI of PSCAR showed faster EUV photospeed with UV-flood exposure, promising early proof-of-principle results of PSCAR, and sensitivity enhancement of PSCAR while the LWR and EL remain almost unchanged. PSCAR system can enhance sensitivity greatly with keeping high resolution (16 nm HP LS is demonstrated).
- The cause of some fluctuation of sensitivity enhancement of PSCAR containing PP-2 among different experimental sites has been investigated. The solution accelerates the implementation of EUV lithography for HVM at the 7 nm node and beyond in addition to further PSCAR material improvement such as new PP material development and further resist formulation optimization.

2-2 One example of precursor(PP) of PS and PS



PP-1

PS



One example of PP and PS and their reaction and UV-Vis spectra

1. The first EUV pattern exposure produces photosensitizers (PSs).

2. Resist has no absorption band at the second flood exposure light wavelength. Therefore, no reaction of resist occurs by only the second flood exposure.

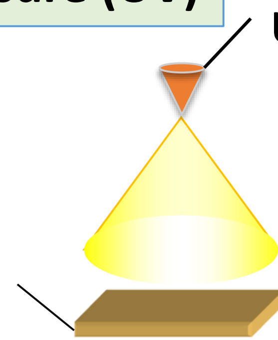
3. Only PSs have absorption bands at the second flood exposure wavelength.

Exposure tools

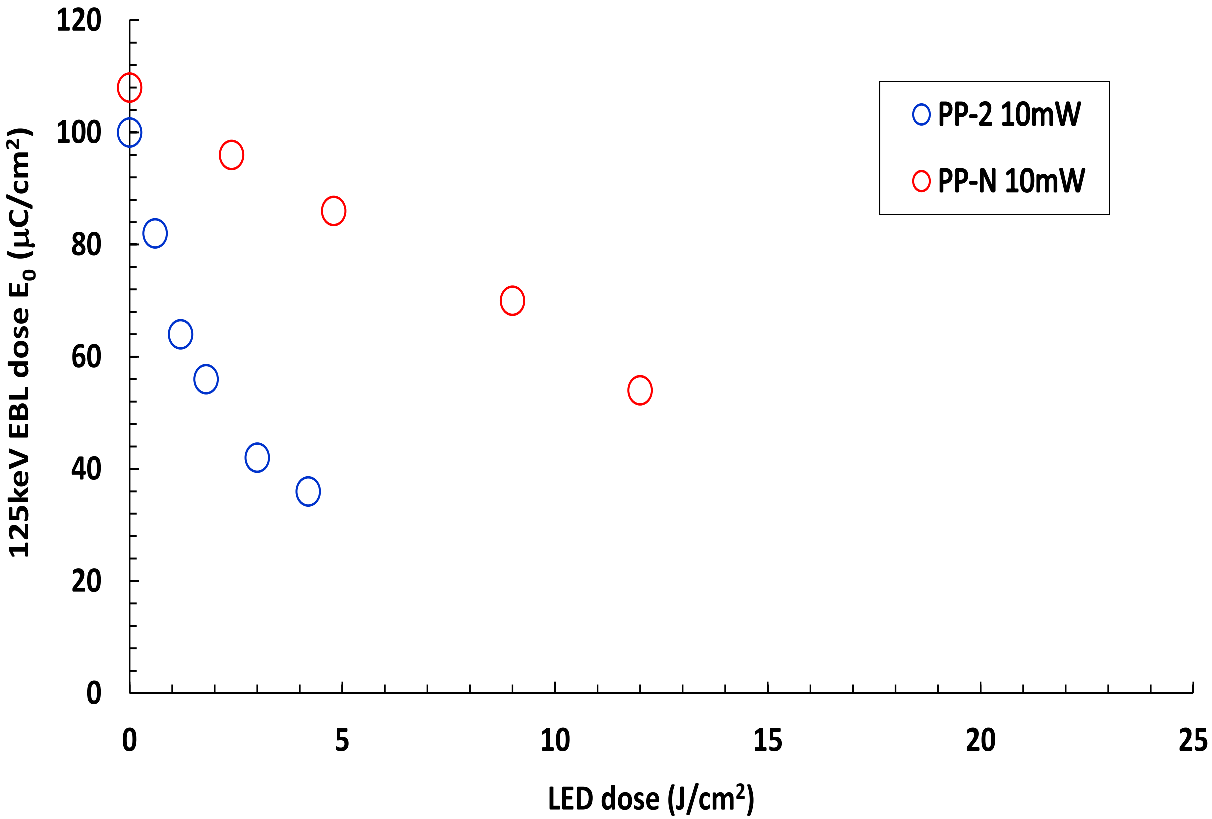
Pattern exposure (EBL)

Elionix ELS-100T (125 keV)

Flood exposure (UV)

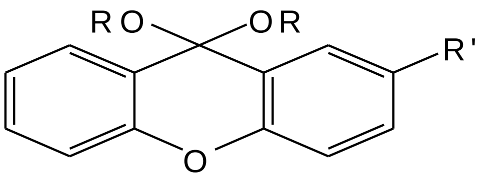


I-215 clean room (Class 1000) 80 m^2



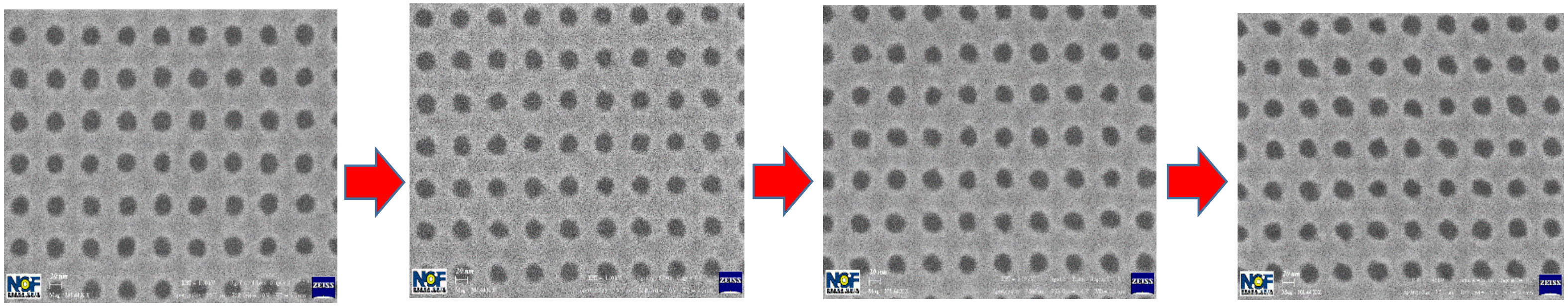
E_0 (EB dose) in 1st 125 keV EB exposure and 2nd 365 nm LED flood exposure. 365 nm LED flood exposure intensity: 10 mW/cm^2

PSCAR in my present talk is CAR + PP. The same CAR made by JSR was used in all experiments in my present talk. Only PP is different. PP-N is a precursor made by Osaka U. and almost same compound of PP-1. PP-2 is a precursor made by JSR and used in five oral presentations at SPIE Advanced lithography 2016.



PP-1

PSCAR
PP-N



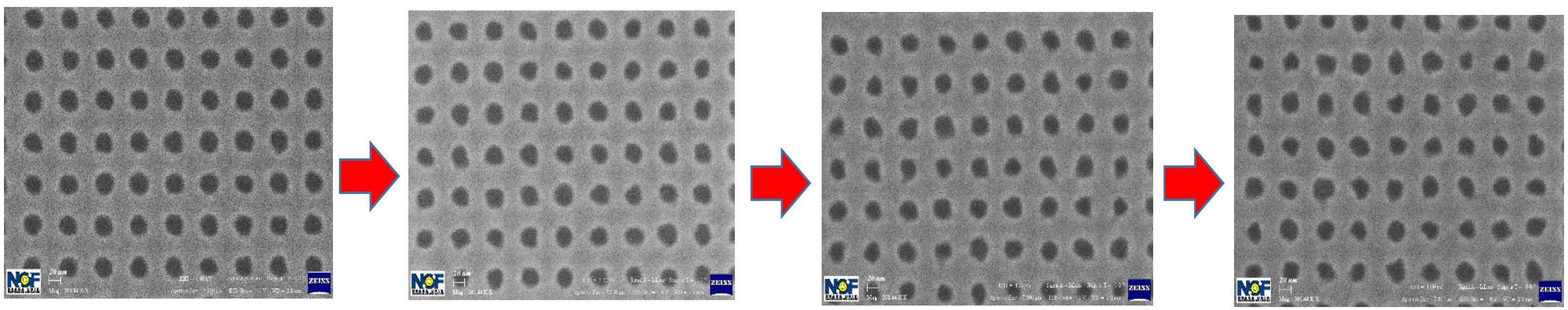
(a) EB only
D:340 μC/cm^2

(b) EB D:320 μC/cm^2
2nd UV flood exposure 2.4 J/cm^2

(c) EB D: 280μC/cm^2,
2nd UV flood exposure 4.8 J/cm^2

(d) EB D: 240μC/cm^2
2nd UV flood exposure 9 J/cm^2

PSCAR
PP-2



(a) EB only
D:340 μC/cm^2

(b) EB D: 240 μC/cm^2
2nd UV flood exposure 1.2 J/cm^2

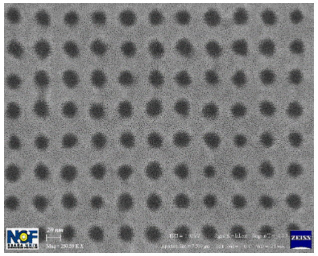
(c) EB D: 160μC/cm^2, 2nd UV
flood exposure 1.8 J/cm2

(d) EB D: 120μC/cm^2
2nd UV flood exposure 3.0 J/cm^2

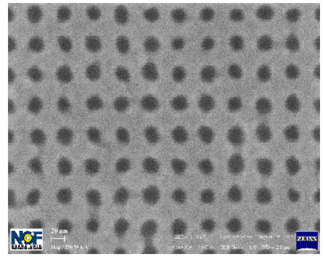
Dense 30 nm hp CH, 125 keV EB pattern exposure, same PSCAR except for PP
UV flood exposure (365 nm, 10mW/cm^2)

PSCAR containing pp-2 has higher sensitivity enhancement rate and also **sensitivity enhancement (>2.8x) for 30 nm hp dense CH patterning.**

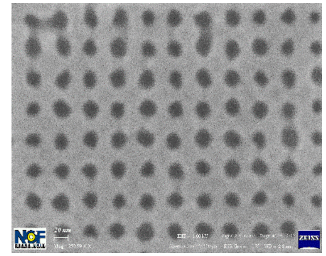
PSCAR
PP-2



(a) EB only
D:400 μC/cm^2

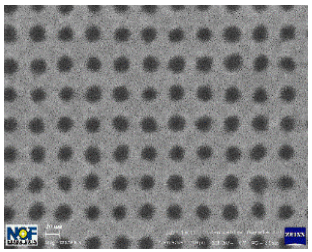


(b) EB D:360 μC/cm^2
2nd UV flood exposure 0.6 J/cm^2

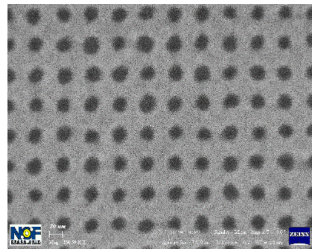


(c) EB D: 340μC/cm^2,
2nd UV flood exposure 1.2 J/cm^2

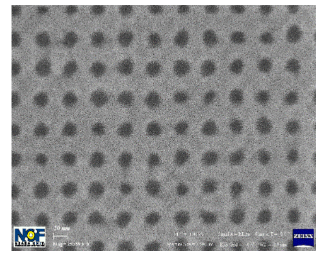
PSCAR
PP-MA



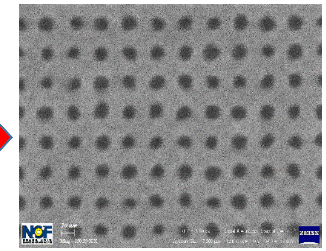
(a) EB only
D:380 μC/cm^2



(b) EB D: 360 μC/cm^2
2nd UV flood exposure 3.0 J/cm^2



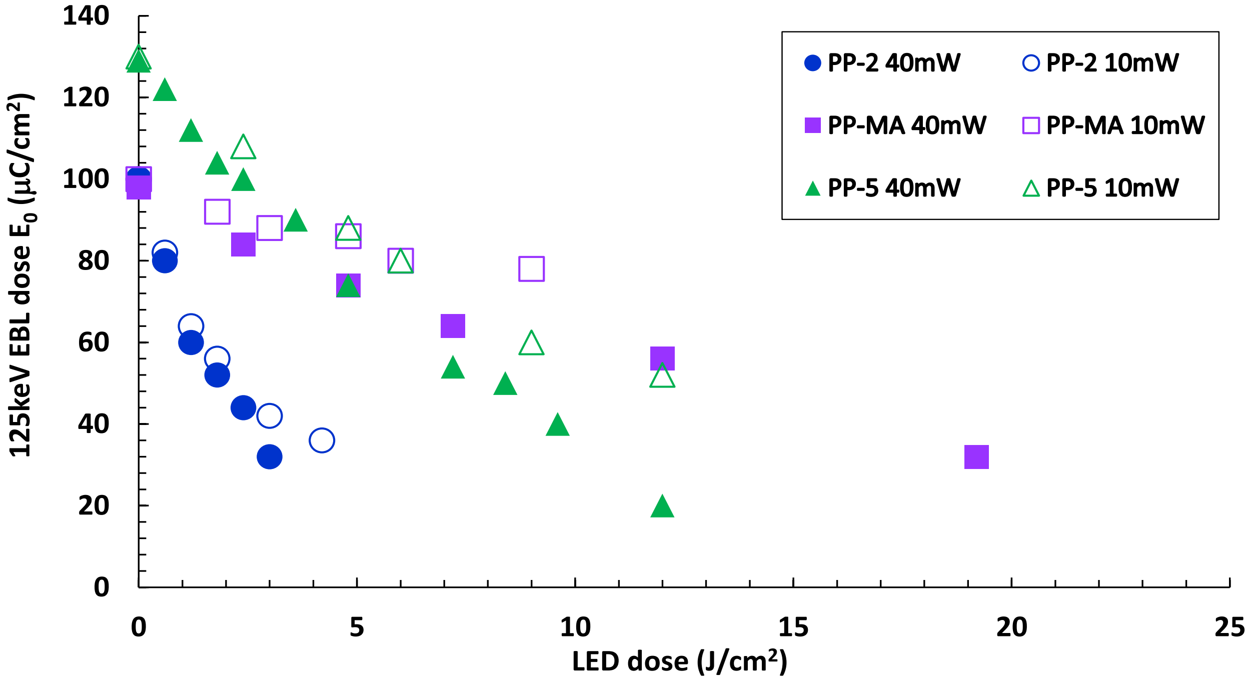
(c) EB D: 340μC/cm^2, 2nd UV flood exposure 6.0 J/cm^2



(d) EB D: 300μC/cm^2
2nd UV flood exposure 9.0 J/cm^2

Dense 20nm CH, 125 keV EB pattern exposure, same PSCAR except for PP
UV flood exposure (365 nm, 10mW/cm^2)

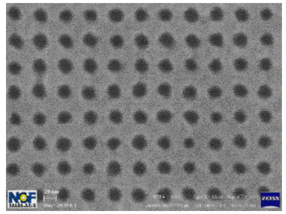
The sensitivity enhancement rate of PSCAR containing PP-2 is larger than PSCAR containing PP-MA (Similar structure but slightly large molecule comparing PP-1 and PP-N)**. However, the sensitivity enhancement of PSCAR** containing PP-2 is smaller than **PSCAR** containing PP-MA.



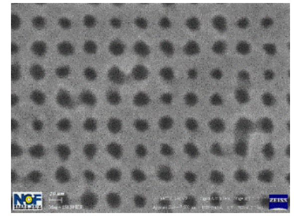
Relation between E0 of EB dose in 1st 125 keV EB pattern exposure and 2nd 365 nm LED flood dose.
365 nm LED flood exposure intensity: 10 mW/cm^2 and 40 mW/cm^2

This figure shows relation between E_0 (1st 125 keV EB exposure dose) and 365 nm LED flood exposure dose. 365 nm LED exposure intensities are 10 mW cm^{-2} and 40 mW cm^{-2}. There is clear post-exposure delay (PED) effect. PED effects are more significant for 10 mW cm^{-2} exposure than for 40 mW cm^{-2} exposure.

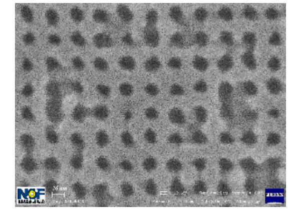
PSCAR
PP-2



(a) EB only D:400 μC/cm2

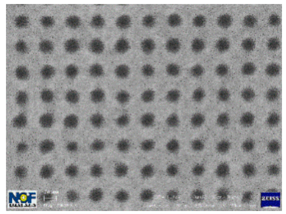


(b) EB D: 260 μC/cm2, 2nd UV flood exposure 1.2 J/cm2

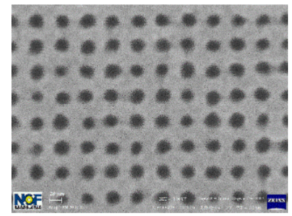


(c) EB D: 220 μC/cm2, 2nd UV flood exposure 1.8 J/cm2

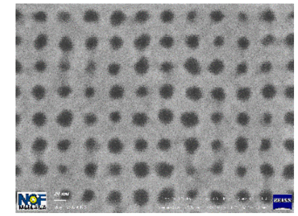
PSCAR
PP-5



(a) EB only D:440 μC/cm2

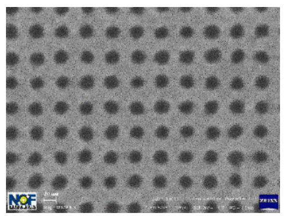


(b) EB EB: 260μC/cm2, 2nd UV flood exposure 6 J/cm2

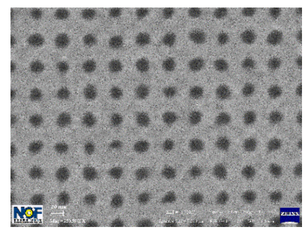


(c) EB EB:200μC/cm2, 2nd UV flood exposure 8.4 J/cm2

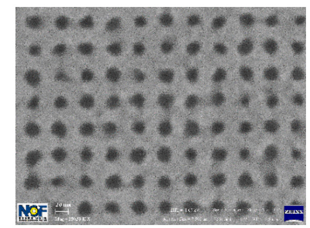
PSCAR
PP- MA



(a) EB only D:380 μC/cm2



(b) EB D:240 μC/cm2, 2nd UV flood exposure 7.2 J/cm2



(c) EB D: 200μC/cm2, 2nd UV flood exposure 12 J/cm2

20 nm hp CH, 125 keV EB pattern exposure,
PSCAR is the same except for PP, UV flood (365 nm, 40mW/cm2) Dense

The sensitivity enhancement rate of PSCAR containing PP-2 is largest. However, the sensitivity enhancement of PSCAR containing PP-MA and PSCAR containing PP-5 is much higher than the sensitivity enhancement of PSCAR containing PP-2.

In the case of PSCAR containing PP-2, pattern degradation depends on 2nd UV flood exposure dose and 1st EB pattern exposure dose, but the dependence of 2nd flood exposure intensity is not clear.

Summary

1. At first, fundamental aspect of PSCAR and how to overcome RLS trade-off were explained.

2. The sensitivity enhancement rate of PSCAR containing PP-2 is largest among PSCARs. PSCAR containing PP-2 is very good for dense 30 nm hp CH patterning by EBL at Osaka University.

3. However, pattern degradation occurs at almost the same low 2^{nd} flood UV exposure dose (1. 2 J cm-2) for 10 mW cm-2 and 40 mW cm-2 flood exposure intensity for dense 20 nm hp CH patterning. There is clear intensity dependence of 2^{nd} flood exposure on PSCAR containing PP-2, while it is smaller than PSCAR containing other PPs.

4. The sensitivity enhancement of dense 20 nm hp of CH patterning for PSCAR containing PP-2 is was lower than PSCAR containing some other PP.

5. There are at least 3 type of important reactions for dense 20 nm CH patterning. The first one concerns postexposure delay (PED) effects suffered from airborne contamination and depends strongly on 2^{nd} UV flood exposure intensity. The second one concerns pattern degradation and does not depend on 2^{nd} UV flood exposure intensity but depend on 2^{nd} UV flood exposure dose and EB pattern exposure dose. Third one concerns sensitivity enhancement of PSCAR and depends on 2^{nd} UV flood exposure intensity.

6. The causes of the fluctuation of sensitivity enhancement of PSCAR containing PP-2 among different experimental sites for higher resolution are due to many factors: environmental effects such as PED because of off-line flood exposure system, flood exposure intensity at the resist surface, sub-reactions such as pattern degradation except for sensitivity enhancement, etc..

Future Improvement Plan of PSCAR

1. The detailed reaction mechanisms including pattern degradation reactions should be made clear for further improvement of PSCAR processes and materials.

2. PED effects will be improved very much by well controlled in-line system because postexposure delay (PED) effects suffered from airborne contamination are very significant in off-line system.

3. Higher intensity of 2nd UV flood exposure improves PSCAR processes very effectively for high resolution patterning than the intensity of flood exposure for EUV-IL experiment reported in SPIE Advanced Lithography 2016

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Thank you for your kind attention.